CALIFORNIA INSTITUTE OF TECHNOLOGY

DIVISION OF CHEMISTRY AND CHEMICAL ENGINEERING
THE CHEMICAL LABORATORIES

MATERIALS RES. LAB.
SEP 1 1989
RECEIVED

Howard K. Birnbaum
Office of the Director
MATERIALS RESEARCH LABORATORY
104 South Goodwin Avenue
Urbana, IL 61801

July 15, 1989

Dear Dr. Birnbaum

Enclosed please find materials accounting sheets for cold fusion experiments conducted here in the period from March 24 to August 1, 1989. No gaseous charging experiments were performed. Two types of electrochemical charging experiments are represented: 1) electrolyses from which photon and neutron emissions were measured (12 expts.), and, 2) electrolyses on which calorimetry measurements were performed (4 expts.) Of course, the total number of experiments performed in this time period was much larger - we have provided acounting sheets for only those experiments described in two publications from this lab: N.S. Lewis et.al., *Nature* 340 (1989) 525, N.S. Lewis et.al. *Science*, submitted for publication. Complete experimental details can be found in these sources.

If any additional information regarding these experiments is required, please do not hesitate to contact me.

Sincerely,

Nathan Lewis RMP

Nathan S. Lewis

PASADENA, CALIFORNIA 91125

MATERIALS USED IN COLD FUSION EXPERIMENTS

PRINCIPAL INVESTIGATOR: Nathan S. Lewis

ORGANIZATION: California Institute of Technology

SHORT DESCRIPTION OF TYPE OF EXPERIMENT:

Electrolysis of D_2O with Pd cathode.

Neutron and photon emission during electyrolysis were monitored and compared with background levels.

RESULTS AND COMMENTS:

Statistically significant fluxes of photons or neutrons during electrolyses were not detected.

I. MATERIALS USED FOR ELECTROCHEMICAL EXPERIMENTS (please complete one sheet for each experiment)

(Experiment #1)	CATHODE	ANODE
MATERIAL	Pd	Pt gauze/foil
PURITY	99.99%	> 99.9%
SOURCE OF MATERIAL	Englehard Inc.	Alfa
PREPARATION		
CAST OR WROUGHT	extruded wire, 0.254 x 0.2 cm	
ANNEALED	not annealed	
ATMOSPHERE		
VACUUM		
SPECIAL TREATMENT	not electrochemically pretreated	
CHARACTERIZATION		
STRUCTURAL	none	
CHEMICAL	none	
BEFORE OR AFTER USE		
METHODS		
RESULTS		
NOTABLE OBSERVATIONS	none	
D/METAL RATIO ATTAINED	unknown	

EXPERIMENT YIELDED

HEAT ________YES ________NO

NEUTRONS ________YES ________NO

TRITIUM ________YES ________NO

HELIUM ________YES ________NO

PHOTONS ________YES __X___NO

I. MATERIALS USED FOR ELECTROCHEMICAL EXPERIMENTS (please complete one sheet for each experiment)

(Experiment #2)	CATHODE	ANODE
MATERIAL	Pd	Pt gauze/foil
PURITY	99.99%	> 99.9%
SOURCE OF MATERIAL	Englehard Inc.	Alfa
PREPARATION		
CAST OR WROUGHT	extruded wire, 0.254 x 0.2 cm	
ANNEALED	not annealed	
ATMOSPHERE		
VACUUM		
SPECIAL TREATMENT	not electrochemically pretreated	
CHARACTERIZATION		
STRUCTURAL	none	
CHEMICAL	none	
BEFORE OR AFTER USE		
METHODS		
RESULTS		
NOTABLE OBSERVATIONS	electrolyte was 50/50 D_2O/H_2O upper limit: $2.2 \times 10^6\ \gamma/cm^3$ Pd/H at 5.5 MeV	
D/METAL RATIO ATTAINED	unknown	

EXPERIMENT YIELDED

HEAT ________YES ________NO

NEUTRONS ________YES ________NO

TRITIUM ________YES ________NO

HELIUM ________YES ________NO

PHOTONS ________YES __X____NO

I. MATERIALS USED FOR ELECTROCHEMICAL EXPERIMENTS (please complete one sheet for each experiment)

(Experiment #3)	CATHODE	ANODE
MATERIAL	Pd	Pt gauze/foil
PURITY	99.99%	> 99.9%
SOURCE OF MATERIAL	Englehard Inc.	Alfa
PREPARATION		
CAST OR WROUGHT	extruded wire, 0.254 x 8 cm	
ANNEALED	300°C x 2 hrs.	
ATMOSPHERE	--	
VACUUM	10^{-6} torr	
SPECIAL TREATMENT	electrochemical pretreatment: 50 mA/cm^2 x 20 min. anodization	
CHARACTERIZATION		
STRUCTURAL	none	
CHEMICAL	none	
BEFORE OR AFTER USE		
METHODS		
RESULTS		
NOTABLE OBSERVATIONS	upper limit: 2.9 x 10^4 n/cm^3 Pd/H	
D/METAL RATIO ATTAINED	unknown	

EXPERIMENT YIELDED	HEAT	________YES	________NO
	NEUTRONS	________YES	__X____NO
	TRITIUM	________YES	________NO
	HELIUM	________YES	________NO
	PHOTONS	________YES	________NO

I. MATERIALS USED FOR ELECTROCHEMICAL EXPERIMENTS (please complete one sheet for each experiment)

Experiment #4)	**CATHODE**	**ANODE**
MATERIAL	Pd	Pt gauze/foil
PURITY	>99.9%	> 99.9%
SOURCE OF MATERIAL	Manufacturer unknown	Alfa
PREPARATION		
CAST OR WROUGHT	hollow cylinder, o.d. = 0.52 cm i.d. = 0.47 cm, l = 2.5 cm.	
ANNEALED	not annealed	
ATMOSPHERE		
VACUUM		
SPECIAL TREATMENT	not electrochemically pretreated	
CHARACTERIZATION		
STRUCTURAL	none	
CHEMICAL	surface elemental analysis	
BEFORE OR AFTER USE	before	
METHODS	energy dispersive X-ray analysis (EDX)	
RESULTS	>99.9% Pd	
NOTABLE OBSERVATIONS	upper limits: 620 γ/cm^3 Pd/H at 5.5 MeV 820 n/cm^3 Pd/H	
D/METAL RATIO ATTAINED	unknown	

EXPERIMENT YIELDED	HEAT	YES	NO
	NEUTRONS	YES	[✓ NO]
	TRITIUM	YES	NO
	HELIUM	YES	NO
	PHOTONS	YES	[✓ NO]

I. MATERIALS USED FOR ELECTROCHEMICAL EXPERIMENTS (please complete one sheet for each experiment)

(Experiment #5)	CATHODE	ANODE
MATERIAL	Pd	Pt gauze/foil
PURITY	99.99%	> 99.9%
SOURCE OF MATERIAL	Johnson Mathey Inc.	Alfa
PREPARATION		
CAST OR WROUGHT	extruded wire, 0.1 x 3.7 cm	
ANNEALED	350°C x 3 hrs.	
ATMOSPHERE	Ar	
VACUUM	--	
SPECIAL TREATMENT	electrochemical pretreatment: $50\ \text{mA/cm}^2$ x 20 min. anodization	
CHARACTERIZATION		
STRUCTURAL	none	
CHEMICAL	surface chemical analysis	
BEFORE OR AFTER USE	after	
METHODS	XPS	
RESULTS	clean Pd surface; no detectable Li.	
NOTABLE OBSERVATIONS	upper limits: $4700\ \gamma/\text{cm}^3$ Pd/H at 5.5 MeV $4.2 \times 10^5\ \gamma/\text{cm}^3$ Pd/H at 23.8 MeV $4700\ \text{n/cm}^3$ Pd/H	
D/METAL RATIO ATTAINED	unknown	

EXPERIMENT YIELDED	HEAT	________YES	________NO
	NEUTRONS	________YES	__X___NO
	TRITIUM	________YES	________NO
	HELIUM	________YES	________NO
	PHOTONS	________YES	__X___NO

I. MATERIALS USED FOR ELECTROCHEMICAL EXPERIMENTS (please complete one sheet for each experiment)

(Experiment #6)	CATHODE	ANODE
MATERIAL	Pd	Pt gauze/foil
PURITY	>99.9%	> 99.9%
SOURCE OF MATERIAL	David Fell Co.	Alfa
PREPARATION		
CAST OR WROUGHT	extruded wire, 0.22 x 10 cm	
ANNEALED	350°C x 2 hrs.	
ATMOSPHERE	--	
VACUUM	10^{-6} torr	
SPECIAL TREATMENT	electrochemical pretreatment: 50 mA/cm^2 x 20 min. anodization	
CHARACTERIZATION		
STRUCTURAL	none	
CHEMICAL	none	
BEFORE OR AFTER USE		
METHODS		
RESULTS		
NOTABLE OBSERVATIONS	upper limits: 470 γ/cm^3 Pd/H at 5.5 MeV 3.4×10^4 γ/cm^3 Pd/H at 23.8 MeV 210 n/cm^3 Pd/H	
D/METAL RATIO ATTAINED	unknown	

EXPERIMENT YIELDED	HEAT	________YES	________NO
	NEUTRONS	________YES	___X___NO
	TRITIUM	________YES	___X___NO
	HELIUM	________YES	________NO
	PHOTONS	________YES	___X___NO

I. MATERIALS USED FOR ELECTROCHEMICAL EXPERIMENTS (please complete one sheet for each experiment)

(Experiment #7)	CATHODE	ANODE
MATERIAL	Pd	Pt gauze/foil
PURITY	>99.99%	> 99.9%
SOURCE OF MATERIAL	Bell Labs	Alfa

PREPARATION
CAST OR WROUGHT
ANNEALED
ATMOSPHERE
VACUUM
SPECIAL TREATMENT

cast wire, 0.25 x 0.8 cm
not annealed.

electrochemical pretreatment:
50 mA/cm^2 x 20 min. anodization

CHARACTERIZATION
STRUCTURAL — none
CHEMICAL — none
BEFORE OR AFTER USE
METHODS
RESULTS

NOTABLE OBSERVATIONS

upper limits:
3200 γ/cm^3 Pd/H at 5.5 MeV
2.9 x 10^5 γ/cm^3 Pd/H at 23.8 MeV
1700 n/cm^3 Pd/H

D/METAL RATIO ATTAINED — unknown

EXPERIMENT YIELDED			
	HEAT	________YES	________NO
	NEUTRONS	________YES	___X___NO
	TRITIUM	________YES	___X___NO
	HELIUM	________YES	________NO
	PHOTONS	________YES	___X___NO

I. MATERIALS USED FOR ELECTROCHEMICAL EXPERIMENTS (please complete one sheet for each experiment)

(Experiment #8)	CATHODE	ANODE
MATERIAL	Pd	Pt gauze/foil
PURITY	>99.999%	> 99.9%
SOURCE OF MATERIAL	Caltech	Alfa
PREPARATION		
CAST OR WROUGHT	cast ingot, ≈0.44 x 0.7 x 2.95 cm	
ANNEALED	300°C x 3 hrs.	
ATMOSPHERE	--	
VACUUM	10^{-6} torr	
SPECIAL TREATMENT	electrochemical pretreatment: 50 mA/cm^2 x 20 min. anodization	
CHARACTERIZATION		
STRUCTURAL	none	
CHEMICAL	none	
BEFORE OR AFTER USE		
METHODS		
RESULTS		
NOTABLE OBSERVATIONS	upper limits: 85 γ/cm^3 Pd/H at 5.5 MeV 1.2 x 10^4 γ/cm^3 Pd/H at 23.8 MeV 110 n/cm^3 Pd/H	
D/METAL RATIO ATTAINED	unknown	

EXPERIMENT YIELDED

HEAT ________YES ________NO

NEUTRONS ________YES __X___NO

TRITIUM ________YES ________NO

HELIUM ________YES ________NO

PHOTONS ________YES __X___NO

I. MATERIALS USED FOR ELECTROCHEMICAL EXPERIMENTS (please complete one sheet for each experiment)

(Experiment #9)	CATHODE	ANODE
MATERIAL	Pd	Pt gauze/foil
PURITY	99.9%	> 99.9%
SOURCE OF MATERIAL	David Fell Inc.	Alfa
PREPARATION		
CAST OR WROUGHT	cast wire, 0.25 x 2.5 cm	
ANNEALED	300°C x 12 hrs.	
ATMOSPHERE	--	
VACUUM	10^{-6} torr	
SPECIAL TREATMENT	electrochemical pretreatment: 50 mA/cm^2 x 20 min. anodization	
CHARACTERIZATION		
STRUCTURAL	none	
CHEMICAL	surface chemical analysis of cathode	
BEFORE OR AFTER USE	after	
METHODS	XPS	
RESULTS	≈4 equivalent monolayers MgO present (presumably from casting crucible) no detectable Li.	
NOTABLE OBSERVATIONS	upper limits: 420 γ/cm^3 Pd/H at 5.5 MeV 3.5 x 10^3 γ/cm^3 Pd/H at 23.8 MeV 200 n/cm^3 Pd/H	
D/METAL RATIO ATTAINED	unknown	

EXPERIMENT YIELDED	HEAT	________YES	________NO
	NEUTRONS	________YES	__X____NO
	TRITIUM	________YES	________NO
	HELIUM	________YES	________NO
	PHOTONS	________YES	__X____NO

I. MATERIALS USED FOR ELECTROCHEMICAL EXPERIMENTS (please complete one sheet for each experiment)

(Experiment #10)	CATHODE	ANODE
MATERIAL	Pd	Pt gauze/foil
PURITY	99.9%	> 99.9%
SOURCE OF MATERIAL	David Fell Inc.	Alfa
PREPARATION		
CAST OR WROUGHT	cast wire, 0.25 x 2.5 cm	
ANNEALED	300°C x 12 hrs.	
ATMOSPHERE	--	
VACUUM	10^{-6} torr	
SPECIAL TREATMENT	electrochemical pretreatment: 50 mA/cm^2 x 20 min. anodization	
CHARACTERIZATION		
STRUCTURAL	none	
CHEMICAL	none	
BEFORE OR AFTER USE		
METHODS		
RESULTS		
NOTABLE OBSERVATIONS	upper limits: 420 γ/cm^3 Pd/H at 5.5 MeV 3.5 x 10^3 γ/cm^3 Pd/H at 23.8 MeV 200 n/cm^3 Pd/H	

D/METAL RATIO ATTAINED 0.804 D/Pd (by direct measurement of D_2 gas volume contained by cathode after electrolysis)

EXPERIMENT YIELDED	HEAT	________YES	________NO
	NEUTRONS	________YES	___X____NO
	TRITIUM	________YES	________NO
	HELIUM	________YES	________NO
	PHOTONS	________YES	___X____NO

I. MATERIALS USED FOR ELECTROCHEMICAL EXPERIMENTS (please complete one sheet for each experiment)

(Experiment #11)	CATHODE	ANODE
MATERIAL	Pd	Pt gauze/foil
PURITY	99.9%	> 99.9%
SOURCE OF MATERIAL	David Fell Inc.	Alfa
PREPARATION		
CAST OR WROUGHT	cast wire, 0.25 x 2.5 cm	
ANNEALED	300°C x 12 hrs.	
ATMOSPHERE	--	
VACUUM	10^{-6} torr	
SPECIAL TREATMENT	electrochemical pretreatment: 50 mA/cm^2 x 20 min. anodization	
CHARACTERIZATION		
STRUCTURAL	none	
CHEMICAL	none	
BEFORE OR AFTER USE		
METHODS		
RESULTS		
NOTABLE OBSERVATIONS	upper limits: 420 γ/cm^3 Pd/H at 5.5 MeV 3.5×10^3 γ/cm^3 Pd/H at 23.8 MeV 200 n/cm^3 Pd/H	

D/METAL RATIO ATTAINED 0.771 D/Pd (by direct measurement of D_2 gas volume contained by cathode after electrolysis)

EXPERIMENT YIELDED

HEAT ________YES ________NO

NEUTRONS ________YES __X___NO

TRITIUM ________YES ________NO

HELIUM ________YES __X___NO
(≈10 mg samples of cathode were vaporized in analysis chamber and analyzed by MS)

PHOTONS ________YES __X___NO

I. MATERIALS USED FOR ELECTROCHEMICAL EXPERIMENTS (please complete one sheet for each experiment)

(Experiment #12)	CATHODE	ANODE
MATERIAL	Pd	Pt gauze/foil
PURITY	99.9%	> 99.9%
SOURCE OF MATERIAL	David Fell Inc.	Alfa
PREPARATION		
CAST OR WROUGHT	cast wire, 0.25 x 2.5 cm	
ANNEALED	300°C x 12 hrs.	
ATMOSPHERE	--	
VACUUM	10^{-6} torr	
SPECIAL TREATMENT	electrochemical pretreatment: $50\ mA/cm^2$ x 20 min. anodization	
CHARACTERIZATION		
STRUCTURAL	none	
CHEMICAL	none	
BEFORE OR AFTER USE		
METHODS		
RESULTS		
NOTABLE OBSERVATIONS	upper limits: 420 γ/cm^3 Pd/H at 5.5 MeV 3.5×10^3 γ/cm^3 Pd/H at 23.8 MeV 200 n/cm^3 Pd/H	

D/METAL RATIO ATTAINED 0.794 D/Pd (by direct measurement of D_2 gas volume contained by cathode after electrolysis)

EXPERIMENT YIELDED			
	HEAT	________YES	________NO
	NEUTRONS	________YES	__X____NO
	TRITIUM	________YES	________NO
	HELIUM	________YES	________NO
	PHOTONS	________YES	__X____NO

MATERIALS USED IN COLD FUSION EXPERIMENTS

PRINCIPAL INVESTIGATOR: Nathan S. Lewis

ORGANIZATION: California Institute of Technology

SHORT DESCRIPTION OF TYPE OF EXPERIMENT:

Electrolysis of D_2O with Pd cathode.

Heat balance measurements were performed.

RESULTS AND COMMENTS:

Statistically significant excess enthalpies were not detected in any experiment.

I. MATERIALS USED FOR ELECTROCHEMICAL EXPERIMENTS (please complete one sheet for each experiment)

(Experiment #1)	**CATHODE**	**ANODE**
MATERIAL	Pd	Pt gauze/foil
PURITY	>99.9%	>99.9%
SOURCE OF MATERIAL	David Fell Inc. Bell Labs	Alfa
PREPARATION		
CAST OR WROUGHT	cast wire, 0.21 x 2.1 cm	
ANNEALED	300°C x 12 hrs.	
ATMOSPHERE	--	
VACUUM	10^{-6} torr	
SPECIAL TREATMENT	not electrochemically pretreated	
CHARACTERIZATION		
STRUCTURAL	none	
CHEMICAL	none	
BEFORE OR AFTER USE		
METHODS		
RESULTS		
NOTABLE OBSERVATIONS	Electrolyte = 0.1 M LiOD/D_2O	
D/METAL RATIO ATTAINED	unknown	

EXPERIMENT YIELDED

HEAT ________YES __X___NO

NEUTRONS ________YES ________NO

TRITIUM ________YES ________NO

HELIUM ________YES ________NO

PHOTONS ________YES ________NO

I. MATERIALS USED FOR ELECTROCHEMICAL EXPERIMENTS (please complete one sheet for each experiment)

(Experiment #2)	CATHODE	ANODE
MATERIAL	Pd	Pt gauze/foil
PURITY	>99.9%	>99.9%
SOURCE OF MATERIAL	David Fell Inc. Bell Labs	Alfa
PREPARATION		
CAST OR WROUGHT	extruded wire, 0.38 x 2.4 cm	
ANNEALED	300°C x 12 hrs.	
ATMOSPHERE	--	
VACUUM	10^{-6} torr	
SPECIAL TREATMENT	not electrochemically pretreated	
CHARACTERIZATION		
STRUCTURAL	none	
CHEMICAL	none	
BEFORE OR AFTER USE		
METHODS		
RESULTS		
NOTABLE OBSERVATIONS	Electrolyte = 0.1 $\underline{M}$ LiOH/H_2O	
D/METAL RATIO ATTAINED	unknown	

EXPERIMENT YIELDED	HEAT	________YES	__X___NO
	NEUTRONS	________YES	________NO
	TRITIUM	________YES	________NO
	HELIUM	________YES	________NO
	PHOTONS	________YES	________NO

I. MATERIALS USED FOR ELECTROCHEMICAL EXPERIMENTS (please complete one sheet for each experiment)

(Experiment #3)	CATHODE	ANODE
MATERIAL	Pd	Pt gauze/foil
PURITY	>99.9%	>99.9%
SOURCE OF MATERIAL	David Fell Inc. Bell Labs	Alfa
PREPARATION		
CAST OR WROUGHT	extruded, machined rod, 0.21 x 2.1 cm	
ANNEALED	not annealed	
ATMOSPHERE		
VACUUM		
SPECIAL TREATMENT	electrochemical pretreatment: 50 mA/cm2 x 20 min. anodization	
CHARACTERIZATION		
STRUCTURAL	none	
CHEMICAL	none	
BEFORE OR AFTER USE		
METHODS		
RESULTS		
NOTABLE OBSERVATIONS	Electrolyte = 0.1 M LiOH, H_2O	
D/METAL RATIO ATTAINED	unknown	

EXPERIMENT YIELDED	HEAT	________YES	__X___NO
	NEUTRONS	________YES	________NO
	TRITIUM	________YES	________NO
	HELIUM	________YES	________NO
	PHOTONS	________YES	________NO

I. MATERIALS USED FOR ELECTROCHEMICAL EXPERIMENTS (please complete one sheet for each experiment)

(Experiment #4)	CATHODE	ANODE
MATERIAL	Pd	Pt gauze/foil
PURITY	>99.9%	>99.9%
SOURCE OF MATERIAL	David Fell Inc. Bell Labs	Alfa

PREPARATION
CAST OR WROUGHT — extruded, machined rod, 0.22 x 2.4 cm
ANNEALED — not annealed
ATMOSPHERE
VACUUM
SPECIAL TREATMENT — electrochemical pretreatment: 50 mA/cm2 x 20 min. anodization

CHARACTERIZATION
STRUCTURAL — none
CHEMICAL — none
BEFORE OR AFTER USE
METHODS
RESULTS

NOTABLE OBSERVATIONS — Electrolyte = 0.1 M LiOD, D_2O

D/METAL RATIO ATTAINED — unknown

EXPERIMENT YIELDED

HEAT	________YES	__X___NO
NEUTRONS	________YES	________NO
TRITIUM	________YES	________NO
HELIUM	________YES	________NO
PHOTONS	________YES	________NO

HARWELL
UK ATOMIC ENERGY AUTHORITY

Solid State Chemistry Group
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B552.12 Harwell Laboratory
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From Dr D E Williams
Group Leader

19th September 1989

Prof H K Birnbaum
Materials Research Laboratory
University of Illinois
104 South Goodwin Ave
Urbana
IL 61801
USA

MATERIALS RES. LAB.
SEP 25 1989
RECEIVED

Dear Prof Birnbaum

"COLD FUSION"

I am responding to your request for information about our work. Rather than fill in your sheets, I thought it preferable to send you a copy of the manuscript which we have recently submitted. This has not yet been accepted for publication: I have been informed that I may send it to you providing you treat it as one would normally treat a preprint. I have not made this freely available because I have become very sensitive to the weight which has been attached to our work and also because of my relationship with Martin Fleischmann and Stan Pons. I wanted to allow them the opportunity to point out to me privately any mistakes which there may be in it. I have not yet heard from them, nor have I had referees' comments back. Therefore, I believe that opinions expressed in it should continue to be somewhat private. The data given on the other hand stands on its merits, and I believe that this is what you are most interested in. The Harwell report referenced is actually not yet complete: I was interested to get referees reports on the paper before doing this.

I also enclose another preprint, from Culham Laboratory, on the "Frascati" type experiment. This is freely available from Dr McCracken as a Culham Laboratory report. In addition to this work we also attempted to detect neutron bursts from cracking deuterided titanium, in two ways. Firstly, U-bend specimen of Ti6Al4V alloy were subjected to stress-corrosion cracking in CD_3OD/DCl, inside the neutron counter. The cracking in this system is supposed to be an intergranular fracture via hydrides precipitated at the crack tip. It is spectacularly rapid (a few minutes to break a specimen ~1mm thick). Secondly, Ti 6Al4V was heat-treated to harden it (950° 1/2 hour, water quench) then electrolysed as a cathode in D_2SO_4 for ~48 hrs to precipitate deuteride needles, then mechanically fractured within the counter. We used our large (44% efficient) detector with the electronics on the five rings of counting tubes reconfigured to pick up bursts. Nothing significant was observed. This work has not yet been written up.

Finally, we collaborated in an experiment lead by Dr John Davies of the Rutherford-Appleton laboratory, in which Pd and Ti cathodes were subjected to high intensity pulsed beams of muons and pions, whilst they were being electrolytically charged. John Davies has prepared a manuscript, of which I have seen a rough draft. I don't know its current status.

I hope that this information is what you need. Please let me know if I can help further.

Yours sincerely

pp J. C. Marshall.
Dr D E Williams

H.10192

Studies of "Cold Fusion" Electrolytic Cells.

D E Williams(1), D J S Findlay(2), D H Craston(1), M R Sené(2), M Bailey(2), S Croft(2), B W Hooton(3), C P Jones(1), A R J Kucernak(1), J A Mason(4) and R I Taylor(1)

(1) Materials Development Division, Harwell Laboratory, U K Atomic Energy Authority, Didcot, Oxfordshire OX11 0RA, United Kingdom
(2) Nuclear Physics and Instrumentation Division, Harwell Laboratory
(3) UKAEA Nuclear Materials Control Office, Harwell Laboratory
(4) Reactor Centre and Centre for Fusion Studies, Imperial College, Silwood Park, Ascot, London, U K.

Experiments utilizing three different calorimeter designs and high-efficiency neutron detection on a wide range of materials showed, for Pd (six different metallurgical forms), no significant heat output (<1% in the most accurate measurements) and for Pd (ten different forms), Ti, Ti6Al4V alloy, TiFe (hydrogen storage material) and "heavy electron metals" (UPt_3 *and* $CeAl_2$) *no statistically significant neutron emission* ($\pm 0.05\ s^{-1}$). *A search for 5.5MeV* γ*s from p-d fusion also showed no effect* ($\pm 0.02\ s^{-1}$). *No* ^4He *was found in Pd cathodes. Spurious effects which, undetected, could have lead to claims of cold fusion, included noise from neutron counters, cosmic-ray background variations, calibration errors in simple calorimeters and variable electrolytic enrichment of tritium. Clear bounds for non-observance of cold fusion have been set, using well-characterised materials under carefully controlled and well-understood experimental conditions.*

Recent publications (1,2) reporting electrochemically induced nuclear fusion, at room temperature, have aroused great interest. The signatures reported are excess heat output, neutron emission and tritium generation from cells with Pd cathodes (1), and neutron emission alone at a much lower level from cells with Ti cathodes (2). Conventional nuclear physics predicts that fusion between light nuclei requires either very high temperature (as in a tokamak) or unusually close proximity of the two nuclei (as in muon catalysed fusion). The calculated fusion rate at the internuclear separation pertaining in the D_2 molecule (0.74A) is $\sim 3 \times 10^{-64} s^{-1}$(3), so the rates reported by Jones et al (2) ($\sim 10^{-23}$/d-d pair/s) are not easy to understand within the context of the known interstititial site separations (~3A), even more so when it is realised that this rate is a severe underestimate because of incomplete deuterium loading in Ti (see below). The reaction rates reported by Fleischmann, Pons and Hawkins (FPH)(1) are even more difficult to understand (4), and the existence, despite strong arguments to the contrary (eg 5), of an unknown mechanism, which results both in an extraordinary enhancement of the reaction rate and a suppression of the normal nuclear reaction channels, has been postulated.

These first claims of the electrolytic cold fusion effect introduced two facts which make replication difficult : firstly that the effect is not consistently reproducible, and secondly that it both takes some time to appear and that it may subsequently disappear. Since electrochemical phenomena can be sensitively affected by the state of the surface, some irreproducibility is not, in itself, surprising, and other recent reports (6,7,8, for example) give well-documented accounts of failures as well as successes (9,10) in observing the claimed effects. Failure to reproduce the effect has been attributed by some (9,11) to the need for rigorous exclusion of H : this is however inconsistent with the postulate of a "fusion" origin for the effect since, at low energies, p-d fusion is expected to be significantly faster than d-d fusion (3). Claims have been made that Pd electrodes must be cast and carefully degassed before use, to remove all traces of carbon and hydrogen impurity (9), or that high current density maintained for a considerable period is an essential feature (10) though it is not completely clear that these latter claims are in fact reproductions of the FPH effect or are of something different. Trace deposition of Pt on the cathode, supposedly causing a lowering of the overpotential for deuterium evolution and hence a lowering of the attainable D level in the cathode, has also been invoked as an explanation for irreproducibility(12). The clear lack of reproducibility necessitates significant replication, with controls at least equal in number to the number of tests if positive results are to be viewed with confidence, and exploration of many different material and electrolyte combinations with good characterisation. Particularly, the timescales and achievable concentrations for electrolytic loading of D into Pd and Ti, the quantities of H "impurity" , and what species are detectable by surface analysis of used cathodes, ought to be determined.

In the process of electrolytic loading of Pd, there will clearly be a concentration gradient, and a moving phase boundary, and the outer atomic layers of the metal will be saturated - possibly supersaturated - with D (13). It might be expected, therefore, that sufficiently sensitive equipment should detect any "fusion" process well before the material is completely loaded. In this work, time scales for H and D loading consistent with the expected diffusion time (x^2/D where the diffusion coefficient, $D = 10^{-7}\text{cm}^2\text{s}^{-1}$ and x is the radius or half-thickness of the specimen) were measured(16) and nuclear counting and calorimetric experiments always went on for much longer than this. The original reports(1,2) did not mention any special precautions to exclude atmospheric water vapour apart from careful covering of the electrolytic cells. Similar procedures were followed here, and it was found that degradation of the heavy water by exchange with atmospheric moisture occurred quite rapidly.

Evolution of hydrogen at a Ti cathode resulted, as is well known (14), in a dense network of hydride precipitates, observable by standard metallographic methods, penetrating below the surface. In 0.1M D_2SO_4 electrolyte at 100mA cm^{-2}, the network penetrated ~30μm in 1hr. Precious metal deposition inhibited the electrolytic uptake, presumably by lowering the overvoltage and promoting gas evolution. Electrolysis in the "brew" used by Jones et al (2) resulted in hydride precipitates confined to the grain boundaries only ; other experiments showed that the presence of $PdCl_2$ in the electrolyte caused this effect, presumably as a consequence of Pd plating on the cathode. It is clear that expressions of the fusion rate which assume that the cathode has composition TiD_2 are completely misleading : metallography shows that the number of d-d pairs is far fewer, hence the claimed fusion rate per d-d pair is far higher than the figure given, and hence the results are even more difficult to reconcile with expectations than had been implied in (2).

In view of the rather large d-d separations in both PdD and TiD_2, it might be argued that "fusion" requires some non-equilibrium state in the lattice - perhaps at the α/β phase boundary in Pd or at the tips of the growing TiD_2 needles or at a lattice defect - where the dd or pd separation could be greatly reduced. In the present work, non-equilibrium situations were created by pulsing the current and fresh dislocations were formed by plastic deformation.

Calorimetry

Three types of calorimeter were employed in this study. Firstly, calorimeters of size and design similar to those used by FPH(1,12)(figure 1a) were constructed. These turned out to be inaccurate instruments with some very subtle sources of error which it is necessary to appreciate and analyse in detail. Sixteen such cells were used, containing different size cathodes (1, 2, 4 or 6 mm Pd rods) and different electrolytes (0.1M LiOD, 0.1M LiOH, 0.1M NaOD or 0.1M NaOH). Figures 2 a&b show the results obtained for a typical cell. An immediately evident characteristic is the sloping baseline, with the sawtooth pattern a consequence of the regular refilling of the cell. The baseline slope can be quantitatively accounted for by a variation with the level of liquid in the cell of the calibration constant, k, given by a combination of the radiative losses through the vacuum jacket (15) and conduction up the glass inner wall of the cell ((16): see figure 2 caption). A consequence of the sloping baseline is that any calibration is only valid for a particular liquid level. These cells were regularly refilled to a reference level at which the calibration had been performed. Figure 2 c shows results for two of the calorimeters at the calibrated liquid level, in the form of percentage excess of apparent output power over the joule input power. There was apparently an endothermic period at the beginning of the run, whose duration increased with cathode diameter. We speculate that this was due to poor stirring of the solution during hydrogen uptake by the cathode causing a temperature gradient in the cell (gas is not evolved at the cathode during this period). Because of this effect, the first 10,000 minutes of data from each cell was excluded in calculating the statistics. Table 1 shows the mean absolute power deviation for each cell and the standard deviation in this value. The standard deviation for all of the H_2O cells was not significantly different from that of the D_2O cells (F test, 1% level) so that the data from all of the cells can be used to estimate the error : $\sigma=0.048$ W (that is ±5-10%). A more detailed analysis of this error(16) showed it to be largely determined by the variability in the liquid level after refilling the cell, but with a contribution also from unquantified variations in the heat loss by conduction up the calorimeter wall to the air above the water bath. In comparison with these errors, effects due to temperature gradients inside the cells were minor. The design used here varied from that in (1,12) in that the glass sleeve which supported the calorimeter and which was in direct contact with the inner wall, provided a large area of thermal contact with the water bath, and thus reduced the effect of the ambient temperature variations.

As expected, occasional points from both H_2O and D_2O cells lay outside the 'control limits' of $\pm 2\sigma$. No points lay outside $\pm 3\sigma$. No cell showed two or more consecutive points outside $\pm 2\sigma$, and the D_2O cells were not different from the H_2O cells in the number of points lying above the control limit. Therefore, it may be concluded that, within the experimental error, there was no significant anomaly in the behaviour of the D_2O cells compared with that of the H_2O cells. If, however, the mean power deviation for all eight of the D_2O cells (+9.91±0.47% or 0.021±0.004W; mean joule input 0.96W) is tested against that for all eight of the H_2O cells (-2.46±0.72% or -0.018±0.004W, mean joule input 0.81W for LiOH cells and 0.61W for NaOH cells), it is clearly highly significant. Since no sequence of individual points lay outside the control limits established above, the suspicion is raised that there is another, unsuspected source of error which scales with the input power. This, of course, could be the postulated 'fusion effect', but the problem is that the magnitude of the effect is commensurate with the errors. The only reliable way of checking is to construct calorimeters which are free of major sources of errors, and in particular the sloping baseline. Both isothermal and steady state (heat flow) calorimeters which satisfy this criterion were therefore also employed in this study (see below).

It has also been possible to analyse in detail the slope of the output curve (16) in order to look for momentary power pulses on time scales shorter than the interval between calibrated points. If the joule input remains constant then this slope should not vary. Any sudden or momentary extra power input,q_c, would change the slope by approximately $(k_{sb}+k_{c,0})q_c/M_0$ (M_0 = water equivalent of the calorimeter, other symbols defined under Figure 2). The number of significant deviations from the mean slope,was found to be roughly the same for both the H_2O and the D_2O cells. For the whole data set, the largest power excursion on a D_2O cell (6 mm rod) was ~45mW and on an H_2O cell (6mm rod) ~40 mW. These are very small in comparison with the input power. It is certainly clear that no unusually large power pulses occurred . Given the difficulties in operating these calorimeters, very occasional occurrences of small fluctuations cannot be considered as support for a 'fusion' hypothesis.

The other two types of calorimeters used in this study are described in Figure 1 and results are given in Table 1. A range of different preparations of Pd and of current density, up to nearly 600 mA cm^{-2}, was explored. With the improved heat flow calorimeters (IHF), the sign and magnitude of the power excess varied with joule input power, but was always less than 5 %. This was within the error bounds (see Table 1). The most accurate calorimeter used was the isothermal calorimeter (minimum detectable power change ~10mW; minimum detectable energy in any brief burst ~40J). Analysis of the results from this was performed at four hour intervals by averaging both the joule input power and the measured output power over a period of approximately twenty minutes. Inspection of the data collected every four minutes between the regions of analysis showed no obvious signs of any short heat 'bursts'. Table 1 shows that other than during the initial charging period of the cast Pd bead electrodes, where a small apparent output power excess (4 - 2%) was observed, the power excess observed on all of the Pd samples was less than 1.5 %. Since similar power excesses (1-0.5%), were also obtained using both Pt cathodes and nichrome wire heaters, it appeared that there was a small systematic error associated with the measurement : if any real excess was observed for the Pd samples it was certainly less than 1%.

2. Neutron Counting

The emission of neutrons from a wide range of cells has been investigated using three different detector systems (Table 2). The large, high efficiency detector with which most of the neutron measurements were made is an oil-moderated assembly of fifty-six ${}^{10}BF_3$ proportional counters configured as five concentric rings (17). The total efficiency for 2.45 MeV d-d neutrons is 44%. An automatic cell shuttle mechanism was constructed to exchange regularly two nominally identical cells, only one of which was powered. This enabled the background and any signal to be counted virtually simultaneously. In operation the cells were exchanged every 5 minutes, and the data from the five rings were recorded separately. Data from a typical run are shown in Figure 3 as differences in the count rate between the powered and unpowered cell. Although in the particular example shown, two spikes can be seen in the count rate differences from the detector as a whole, it is clear that these spikes are due entirely to the misbehaviour of ring 4, and are therefore spurious.

The details of the cells and results of the measurements are given in Table 2. The measured neutron yields are given both as emission rates and as rates per gram and per cm^2 of cathode where appropriate. The neutron emission rate limits are several orders of magnitude below the rates of $\sim 10^4 s^{-1}$ reported in (1) and about one order of magnitude below the rate of $\sim 0.4\ s^{-1}$ claimed by (2). It is significant that the limits in our work were also obtained for cells in which cold fusion could be expected to be enhanced, in particular by using titanium cathodes in the form of a large (40 g) mass of porous granules to increase both the reaction volume and the surface area, and an electrolyte specifically chosen to promote deuterium loading into the cathode (14). As discussed in the introductory section, results have not been expressed in terms of the number of deuterium pairs within metallic lattices.

Since the net count rates given in Table 2 are differences between much larger background rates, runs were undertaken with a calibrated ${}^{252}Cf$ source emitting 0.09 ± 0.01 neutron s^{-1} and a physically identical blank. The result was a satisfactorily agreeing 0.14 ± 0.05 neutron s^{-1}. Furthermore, the expected neutron output of the unpowered UPt_3 cell, due to spontaneous fission of ${}^{238}U$, was 0.22 s^{-1}. The value measured in comparison with an empty cell was $0.20 \pm 0.06\ s^{-1}$. It can be seen that confidence in the results of the shuttle differences is justified.

Measurements on $CeAl_2$ and UPt_3 cells were included in the forlorn hope that high effective electron masses corresponding to these metal crystal lattices would mimic in some way the fusion enhancement effect of "heavy electrons" such as muons in binding the deuterium nuclei closer together. The Pd ribbon run with the cell power switched on and off every 2 hours (which was about eight times the characteristic diffusion time in the ribbon) was undertaken to enhance the appearance of non-equilibrium effects, and results are given in Figure. 4.

3. Gamma counting

Since it has been shown that cold p-d fusion is expected to proceed at rates greater by ~8.5 orders of magnitude than d-d fusion, (3), an alternative investigation of electrolytic enhancement of hydrogen iostope fusion can be carried out by looking for the $D(p, \gamma)^3He$ 5488 keV gamma-rays from p-d fusion. A lead-shielded 113 cm^3 n-type high-purity germanium (HPGe) crystal gamma-ray spectrometer was used to search for any gamma-rays emitted by a variety of cold fusion cells operating with a mixture of light and heavy water. The results, also given in Table 2, are consistent with no gamma-ray emission. Jones et al. (2) report that the fusion activity may last for only 4-8 hours and begin ~1 hour after the cell is powered, and in these circumstances typical values for the errors in the gamma-ray emission rates are ~0.05 s^{-1}. Post-run analysis of the hydrogen isotopes taken up by the cathode with the mixed light and heavy water electrolytes used gave very satisfactory D:H ratios, lying in the range 1.5 - 2.5. It is worth noting that if the proposed enhancement of the fusion process is as valid for p-d as for d-d fusion then because of the enhanced tunnelling in the lighter d-p system (3) the gamma-ray measurements actually provide a much more stringent limit on the cold fusion process than the neutron measurements.

Tritium enrichment

FPH (1) claimed a tritium production rate of about 10^4atoms/s, commensurate with their claimed neutron emission rate. They used a differential technique in which the tritium accumulation in a cell with a Pd cathode was compared with that in a cell with a Pt cathode. They also used a method in which samples were taken for analysis at regular intervals and the total electrolyte volume was maintained constant by addition of fresh D_2O.

Electrolytic enrichment is widely employed to increase the concentration of T in water prior to analysis (18,19). Repeatable results require careful control of the electrolysis, since the enrichment factor can vary widely (18,20,21) : important effects are seen with change of electrode materials, and with variation in the condition (activity) of the electrode surface, with the current density (overvoltage) and with the temperature. Without precautions, the variations in enrichment factor can be more than a factor of two (21). The claims therefore need to be assessed against this known background of variable electrolytic enrichment. Surprisingly, FPH (1) claimed that there was no electrolytic enrichment in their Pt cell.

If the rates of electrolytic evolution of hydrogen isotopes are written as follows

$D_2O \dashrightarrow D_2 + 1/2\, O_2$ rate = r
$DTO \dashrightarrow DT + 1/2\, O_2$ rate = XSr

where r denotes the electrolysis rate, S the TD separation factor and X the mole fraction of tritium in the solution, then the tritium accumulation is given by (16)

$$\frac{X}{X_0} = \frac{1}{(S + \alpha + \gamma)} \left\{ 1 + \alpha + \gamma - (1 - S)\exp\left[- \frac{(S + \alpha + \gamma)rt}{N_0} \right] \right\}$$

----- (4)

where the the total solution volume is maintained constant by addition of fresh D_2O (containing mole fraction X_0 of tritium), the sampling rate of the solution is αr and γr denotes the rate of evaporation of the solution - a small correction which may be calculated assuming that the electrolysis gases passing out of the cell are saturated with water vapour. On the time scales of interest, variability in S would give a variable enrichment

$$\delta\left(\frac{X}{X_0}\right) = - \frac{rt}{N_0}\,\delta S$$

----- (5)

If the solution becomes contaminated by H absorption from the atmosphere, then if S_{obs} denotes the apparent TD enrichment factor derived from the application of equation 4,

$S_{obs} = S / [0.5(1 + f)]$ where $f = (1-X_H) / (1 + X_H(S_{HD} -1))$ ----- (6)

with X_H denoting the mole fraction of H, and S_{HD} the HD separation factor (relative rate of reaction of HDO and D_2O). Therefore, as well as the inherent variability from one electrode to another, it is evident that any variability in the amount of H pickup will give a variation in the apparent enrichment factor :

$$\frac{dS_{obs}}{dX_H} = \frac{S_{HD}}{2\,[\,1 + X_H(\,S_{HD} - 1\,)^2\,]}$$

----- (7)

We found that, unless exceptional precautions were taken (and we believe that we used experimental procedures very similar to those employed by FPH(12)), values of $X_H \sim 0.07$ were common . Under these conditions, a change of X_H of only 0.01 would give a change in S_{obs} of 0.02, which could be significant in the light of the smallness of the claimed effect.

Any assessment of whether differential enrichment can be considered to account for the results given by FPH depends critically on the value of X_0 , which was not reported. Using values (1) of r (1.24×10^{18} atom/s) and N_0 (14.6×10^{23} atom) we calculate from eq. 5 that if X_0 were at the extreme low end of the range for commercial D_2O (3Bq/ml), a value of $\delta S = 0.46$ would be required ; if it were moderate (10 - 15Bq/ml) a value $\delta S \sim 0.1$ would be needed; if it were high (80Bq/ml) $\delta S \sim 0.02$ would suffice.

The applicability of equation 4 was confirmed experimentally, on both Pt and Pd cathodes, in conjunction with calorimetric and neutron counting experiments (16). The fit of this equation to all the experimental data gave, for Pd, $S_{obs} = 0.59$, and for Pt, $S_{obs} = 0.61$. Correction for the uptake of H, using $S_{HD} = 6$ (21), gave $S \approx 0.48$, in line with previous work and theoretical expectations ($S = 0.46 \pm 0.02$, (18,20,21)). For individual electrodes, S_{obs} for Pd varied from 0.46 to 0.65 (corrected S from 0.42 to 0.58), whilst S_{obs} for Pt varied from 0.56 to 0.85 (corrected S from 0.43 to 0.69) - a total range for individual electrodes of $\delta S_{obs} = 0.4$, enough to account for the results of FPH.

It is clear from these results and discussion that more evidence needs to be presented before the tritium accumulation reported by FPH can be considered as experimentally reliable evidence for the occurrence of a fusion process .

Materials Characterisation

With 125μm Pd foils, hydrogen loadings (determined (16) by hot-extraction mass spectrometry c specimens frozen in liquid nitrogen, and independently by electrochemical extraction) of H/Pd = 0.95±0.05 were achieved in ~1hr at $100mAcm^{-2}$ in 0.1M LiOH solution with a Pt anode. The limi of D loading in 0.1M LiOD was lower (0.84±0.03). Rods (1 and 2mm diameter) polarized for extended periods in neutron counting and calorimetry experiments showed D/Pd = 0.76±0.06. That the equilibrium pressure for a given D loading is higher than that for the same H loading is well known (13). Current interruption methods confirmed that overpotentials in the range 0.8 - 1V(1) were being obtained. From an initial composition >99.9% D_2O, the solutions degraded to ~98.5% in 24hr and to 88-98% following electrolysis for many weeks. The resulting ratio H/D in the Pd was 0.02-0.04.

During electrolysis, all of the Pd cathodes became covered with a layer which varied in appearance from a dull tarnish to a dense jet black. In the latter case, loose black material was also formed, which in extreme cases spalled off during electrolysis, giving quite heavy erosion of the cathode. The layer itself evidently represented a modification of the morphology of the cathode at the surface. The formation of a thick black layer was enhanced at high current density, at high temperature, on smaller diameter wire and by frequent abrupt alterations of the current density, repeated over a long period. The layer was more noticeable on the outside of a spiral wound cathode than on the inside.These observations find a natural explanation in an old notion (13) that microfissures, or rifts, develop in Pd as a consequence of heavy loading with hydrogen, in order to release the mechanical strains resulting.

Lithium was present in the surface layer on cathodes used in LiOD, and analysis by SIMS (secondary ion mass spectrometry) apparently showed a concentration profile extending about 1μm into the metal. However, SIMS images showed that the Li was not uniformly distributed, and it seemed likely that it was trapped in microfissures in the surface layer.

Surface analysis showed a number of other species on and in the surface layer, notably small quantities of Pt and traces of Cu, Zn, Fe, Pb and Si : Pt would have originated from the anode and Si from the glass container. No doubt the majority of the other contamination would have come from the solution : the levels found (a few atom % confined to the surface layers) were consistent with deposition by extended electrolysis from a solution of concentration around 10^{-9} - 10^{-10}M. One possible criticism is that low levels of such deposition could poison any essential catalytic activity : pre-electrolysis was applied, therefore, in several experiments, in an attempt to lower the surface contamination. Either repeat experiments were made on the same solution, simply changing the cathode, or the solution was treated beforehand in a separate cell. These procedures were applied both to calorimetric and to nuclear counting experiments.

Because of claims that an unusual mechanism might lead to nuclear reactions proceeding predominantly non-radiatively to ^{4}He, four cathodes (Table 2, first four entries) were analysed by vacuum fusion / mass spectrometry. The high vapour pressure of Pd at the melting point caused difficulties, so internal standards were prepared by ion implantation of 10^{13} and 10^{15} atoms of ^{4}He into samples cut from the cathodes. Detection limits for ^{3}He and ^{4}He determined in this way were ~8x10^{10} atoms/sample - (1 -10)x10^{11} atoms/g. None was found. The expected level if fusion at the FPH rate had been occurring was ~10^{16}atoms/g.

5. Discussion

The current interest in cold fusion has generated a large number of neutron counting experiments. It is well known in counting measurements that in general it is inadvisable to measure signal+background and background at different times and in different physical locations (as in (1)), especially in low count rate experiments, principally because of unexpected systematic variations. A particular problem is in compensating for variation of the background rate and in assessing appropriate errors for the procedure chosen: the work of Jones et al (2) can be criticised on this score (22). It is further notable that in (2), only one run in fourteen showed a significant effect and then only because this particular run was assigned a smaller counting error than the others. In the present work, we have attempted to minimise, by the shuttle procedure, uncertainty about background and counter variability and about error calculation. Given some of the more spectacular claims that have been made, we note that further caution is advisable because of the notorious sensitivity of $^{10}BF_3$ and ^{3}He proportional counters to humidity and of counter/amplifier systems to earth loops. Since in the present work the neutron detectors were segmented, and the relationship between signals from the segments was well known, spurious effects giving inconsistent signals from the segments could be identified.

Some explanations of the apparent excess heat production have emphasised recombination processes at catalytic metal surfaces (23) : however, apart from occasional explosions which did not result in any neutron emission, we found, in agreement with others (15), that this was not a significant effect. Recombination in the gas space above the liquid, either on exposed cathode surface or catalysed by colloidal metal particles eroded from the cathode, might however account for some of the observations of bursts of heat recently reported (24). In discussion of the claims (1), we prefer rather to focus on characteristics of the 'simple' FPH calorimeters, since it is notable that small effects, at the level of the inherent uncertainties, which might mistakenly be claimed as arising from cold fusion, have only been observed in the present work in the one type of calorimeter (FPH type) which has major calibration difficulties. Cells employing the same electrode and electrolyte materials operated in calorimeters which did not have these problems exhibited none of these effects.

FPH (1) describe calibration using the internal resistance heater, by measurement of Newton's law of cooling losses. Typically, this procedure might involve the application of power to the heater, whilst electrolysis was carrying on, following the temperature-time trace until steady state was obtained, then switching the heater off and following the cooling curve. This procedure gives an approximation to the differential calorimeter constant, $k_d = d(\Delta P)/d(\Delta T)$, at the operating temperature of the cell and can give rise to errors in two ways. Firstly, since any calibration sequence would require a time of 5 to 10 hr, extrapolation would be required to obtain the correct value at the reference liquid level : an estimated error of 20% or more could result . Furthermore, because the evaporation of the cell contents increases markedly with increasing temperature, the baseline slope would increase with increasing temperature and the effects of this sort of error would become correspondingly more marked: the claimed effects were indeed greatest in the cells run at the highest input power. Secondly these calorimeters are non-linear (eq 1, fig 2 caption), with the effect being significant when the temperature gradient is large: they cannot be described by a simple Newton's law of cooling constant. If a differential calorimeter constant is used to derive the input power, the calculated output would be (from eq 1, Figure 2 caption)

$$P_{app} = k_d \Delta T = (k_{sb,0} + k_c)\Delta T + 3(k_{sb,0}/T_0)(\Delta T)^2$$

so that, in comparison with the correct output (equation 1)

$$P_{app} - P = 3k_{sb,0}(\Delta T)^2/2T_0$$

If the power applied to the heater is significant in comparison with the electrolysis power then this error will be even greater. Back calculation from the data given in (1) shows that the claimed effects were largest for joule input powers on the order of 6W. For our FPH-type calorimeters, this would have given ΔT~50-60C. Therefore, had these cells been calibrated in this way, an apparent heat excess on the order of 0.8 to 1W would have been observed. The method of calibration employed in the present work (see Figure 1 caption) considerably reduced the effect of these sources of error. The original report (1) was clearly preliminary in nature, and it is evident from the above that the claims made therein cannot be assessed in the absence of a detailed description of the experimental procedure used and of the methods employed to compensate for the systematic errors inherent in the use of a simple calorimeter.

We feel that the present work has served to establish clear bounds for the non-observance of cold fusion in electrolysis cells, under carefully controlled and well understood experimental conditions and incorporating well-characterised materials. Further details can be found in (16). Claimed observations of cold fusion ought now to meet similar standards of data analysis and materials characterisation so that a proper assessment can be made.

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Acknowledgements

This work was financed by the Underlying Science programme of the UKAEA, the UK Department of Energy and the Commission of the European Communit~~ies~~y. We should like to thank Johnson-Matthey plc (Dr I McGill and Dr M Doyle) for much assistance and for the loan of special samples of Pd. IMI Titanium plc (Mr J R B Gilbert) provided Ti and much useful information. We are grateful to the following for valuable assistance : P Fozard and M Newman (H, D and He in Pd), J Monahan (isotopic purity of D_2O), R Morrison (T in D_2O), H Bishop, V Moore and colleagues (surface analysis and microscopy), J Asher (ion implantation), P W Swinden and A M Leatham (construction of shuttle mechanism), R A P Wiltshire (low level ^{252}Cf sources), D A Webb and J O W Norris (computer software), R Roberts (supply of D_2O), R Crispin, C Westcott and R Neat (general assistance) and D Robinson, H Watson and G McCracken (Culham Laboratory - supply of Pd and Pd/Ag, and gas-phase deuteriding of Pd). The newsletters circulated by Dr D Morrison (CERN) were most informative. We should like particularly to acknowledge valuable discussions with Dr D Schriffrin (Southampton University), and Dr P T Greenland, and to thank Dr R Bullough for unwavering support.

TABLES

Table 1

Calorimetry results

Table 2

Measured Neutron and Gamma-ray Emission Rates for Cold Fusion Cells.

FIGURES

Figure 1

Schematic diagram of the three types of calorimeters employed in this study: *a)* FPH type heat flow calorimeters *b)* Improved heat flow (IHF) calorimeters *c)* Isothermal calorimeter.

Methods

The two types of heat flow calorimeter were operated in a water bath at a constant temperature of ~20C (±0.08C). In both cases the cells comprised a spirally wound Pt wire anode (0.25 mm) and a central Pd cathode (Johnson Matthey). For the FPH cells the different electrolytes were prepared either using conductivity water (H_2O cells) or slightly tritiated D_2O (specific activity 13 kBq ml^{-1}) of isotopic purity initially >99.9% . 0.1 M LiOD (D_2O from Aldrich, measured >99.9% initial isotopic purity) was used as the electrolyte in the IHF calorimeters. The Pt and Pd contact wire was shrouded in glass tubing in the IHF cells to prevent any possible catalytic recombination of the electrolysis products. Later experiments with the FPH cells also employed screened electrode contacts, but this had no effect on the results obtained. For both types of heat flow calorimeter the temperature of the cell contents was measured using one or more thermistors, which were either glass clad and immersed in the cell (FPH calorimeters), or positioned inside a tightly fitting aluminium can surrounding the cell (IHF calorimeters). The aluminium can defined an isothermal surface for conduction of heat away from the cell, and its use as the temperature measurement surface eliminated the sloping baseline problem of the FPH cells. The IHF cells contained a Pd wire electrode insulated to the very tip which was positioned about three quarters of the way up the cell. This was used to define the internal liquid level during filling, or refilling, of the cell. The larger volume of electrolyte in the IHF cells (300ml) meant that refilling was required only occasionally, but the large thermal mass resulting meant that the response was slow (time constant ~12hr) : thus they were not sensitive to small bursts of heat. Calibration of the heat flow calorimeters was performed using a nichrome wire heater placed in an oil filled glass tube which was in contact with the cell contents. The calibration procedure involved operating the heater, either without electrolytic current, or with a current significantly less (0.2-0.4 times) than the normal electrolysis current, until a steady state temperature was attained. With the FPH cells, use of a lower electrolysis current secured stirring whilst at the same time diminishing the errors arising from the baseline drift, and prior to each individual calibration the cells were refilled. An empirical calibration curve was thus obtained by fitting the observed thermistor resistance, R, to a range of applied powers, P, using the equation

$$P = a - b(\log R) + c(\log R)^2$$

The standard error of estimate on the fitted curve varied from approximately 10 to 70mW, largely reflecting the error in extrapolation to the reference level. Neutron counting was performed in conjunction with the operation of the FPH cells (16). Detection sensitivity was 3 events/s in the cell. No signal above background was ever observed.

The isothermal calorimeter [25] comprises three concentric aluminium cylinders each separated by a heat transfer medium with a relatively low thermal conductivity. The cylinder temperatures are maintained by electrical heaters wound as helical coils around each cylinder. Temperature control is achieved by resistance thermometers on each cylinder which are used in conjunction with classical control software and the cylinder heaters. The rate of thermal energy evolution in the measurement chamber is determined by precisely measuring the electrical power supplied to the chamber. The calorimeter is operated at a measurement chamber temperature of 42±0.001C. The measurement chamber power resolution is less than 5 mW for an operating power of 20W. The electrolytic cell contained ~1 litre of 0.1M LiOD. The cathode was contained in a perforated glass canopy to prevent the evolved gases from mixing inside the measurement chamber. The cell was thermally coupled to the calorimeter measurement chamber by conducting oil. The measured output power of both the isothermal and IHF cells was corrected for the power loss due to evaporation of the electrolyte, assuming that the electrolysis gases were saturated in water vapour as they passed out of the cell (25.0mW/A at 42C) : $q_v = (p_v/p_0)(1.5)\Delta H_v I / (2F)$ where p_v denotes the saturation vapour pressure and ΔH_v the latent heat of evaporation of the electrolyte, p_0 is the atmospheric pressure and F the Faraday constant (assumes ideal gases).

Figure 2

a) Raw data from a FPH type calorimeter containing a 4 mm Pd rod (1.5 cm long, Johnson Matthey "specpure", drawn from sintered stock) in LiOH electrolyte. The two lines represent -1- the joule input power to the cell - $P_{in} = I(V-V_0)$ where $V_0 = \Delta H_d/2F$ (1.527V for D_2O and 1.481V for H_2O , ΔH_d being the enthalpy of dissociation, eg $D_2O(l) \rightarrow D_2(g) + 1/2O_2(g)$) and

-2- the output power calculated from the thermistor reading.

b) An expanded region of (a), which emphasises the sloping baseline. The line -3- is the gradient of the apparent output power calculated by differentiation of the data using a 7 point Savitsky-Golay routine [26], stepping one point at a time. At points -a- the calorimeter was topped up to the reference mark with H_2O pre-warmed to the cell temperature. At points -b- a volume of liquid estimated from the electrolysis rate was added.

c) Results for the two most consistently exothermic calorimeters - 2mm x 3cm Pd rod in (i) LiOD and (ii) LiOH- in the form of percentage excess of apparent output power over the joule input power. The error bars represent the control limits $\pm 2\sigma$ calculated from the results obtained for all the different cells -see text.

d) Raw data obtained using the isothermal calorimeter (2cmx2mm diameter Pd cathode), immediately following the application of the input power, with the line representing the joule input power and the dots the observed cell power. The response time of this calorimeter is governed by the time to obtain thermal mixing of the cell contents, and is faster than that of the simple calorimeters, despite the large solution volume.

Sloping Baseline

The response of the 'simple' FPH calorimeter can be modelled by (16):-

$$P_{in} = k\Delta T = (k_{sb} + k_c)\Delta T \qquad (1)$$

where (15),

$$k_{sb} = \sigma A_1[T_i^4 - T_0^4] \approx 4\sigma A_1 T_0^3[1 + 3\Delta T/2T_0] = k_{sb,0}(1 + 3\Delta T/2T_0) \qquad (2)$$

and (16)

$$k_c \approx \kappa A_2/l = \kappa A_2/(l_0 + IV\,\delta t/2F\pi r_i^2) \approx k_{c,0}(1 - \alpha\delta t) \qquad (3)$$

(P_{in}= joule input power, k=calorimeter constant, k_{sb} & k_c being the contributions to the calorimeter constant of radiative losses through the vacuum jacket and conduction up the glass inner wall respectively, σ = Stefan-Boltzmann constant, A_1 = contact area of the solution with the wall of the cell, T_0 = bath temperature, T_i = cell temperature, $\Delta T = T_i - T_0$, κ = thermal conductivity of the glass, l = the distance from the liquid to the point where the inner glass wall comes into contact with the bath - initial value l_0 - A_2 = cross sectional area of the inner glass wall, I= cell current (300 mA), V = molar volume of cell solution, δt = elapsed time after refilling the cell, r_i = internal radius of the glass vessel and $\alpha = IV/2F\pi r_i^2 l_0$). The calorimeter constant for the cells was observed to be around 0.1 W/K, with calculation using equation (2) suggesting roughly equal contributions from k_{sb} and k_c. A more complete description of the calorimeter should also take into account the effects of the solution loss on the heat capacity of the calorimeter. It can be shown however that the contribution of this to the sloping base line is insignificant (16).

Figure 3

Data from a typical run on the large high efficiency neutron detector. These show the differences between powered and unpowered cell count rates resulting from successive alternate shuttle positions for 40g of titanium granules. In addition to results from the detector as a whole, results from the five rings of 2 inch diameter 107 cm active length $^{10}BF_3$ proportional counters are also shown. A 90 mm diameter through-tube passes through the detector, and the shielding consists of 6 inches of borated resin, 1 mm of cadmium and 2 inches of lead. The neutron detection efficiency is high and is largely independent of neutron energy, varying from 48% for 0.5 MeV (Am/Li) neutrons to 40% for 4.2 MeV (Am/Be) neutrons. The background count rate is 4 - 5 counts s^{-1}, mostly neutrons from cosmic rays. Each of the five rings of counters has its own independent pre-amplifier, pulse -shaping amplifier and discriminator, and the mean energy of neutrons counted can be obtained from the ratio of counts in the outermost ring of counters (ring 5) to counts in the innermost (ring 1). The pre-amplifiers and the EHT filters and fan-outs are all contained within a desiccated electrically screened box, and earth loops and induced electromagnetic pick-up ("aerial") effects from external coaxial cable runs to the PDP-11/45 data acquisition computer are eliminated by using isolating high frequency pulse transformers and ferrite chokes. The neutron detector and its immediately associated electronics are located in a temperature-controlled air-conditioned blockhouse with 2 foot thick concrete walls and roof.

Figure 4

Time dependence of neutron emission from an electrolytic cell with melt-spun Pd ribbon cathode and Pd foil anode, with power alternately turned on for deuterium loading and off for relaxation every 2 hours by the data acquisition computer : see Table 2 note u. The total length of the run was 110 hours, and the sums of the "on" and "off" data are shown. This run was undertaken to enhance the appearance of the non-equilibrium effects discussed in the introductory section. It is assumed that the ribbon would have had a high density of grain boundaries, dislocations and other lattice defects. Since the 'on' and 'off' periods were several times the characteristic diffusion time for the ribbon, it is assumed that the composition was cycling in the β-phase region between the fully-loaded condition (D/Pd ≈ 0.83) and the limit of the (α+β) phase field (D/Pd ≈ 0.65).

TABLE 1 - Calorimetry Results

Calorimeter Type	Cathode Material	Electrolyte	i/mA	~ Surface Area /cm²	~ Volume/cm³	~i/mAcm³	Mean input[a] Power/W	Excess Power /mW[b]	% Excess[c]	~ Charging time (hours)
PFH[r]	6 mm Pd Rod[d]	0.1M LiOD	300	3.9	0.283	78	0.96	12 ± 57	1.25	870
		0.1M LiOH	300	3.9	0.283	78	0.82	-45 ± 50	-5.49	870
		0.1M NaOD	300	3.9	0.283	78	0.98	57 ± 44	5.82	870
		0.1M NaOH	300	3.9	0.283	78	0.59	14 ± 71	2.37	870
	4 mm Pd Rod[d]	0.1M LiOD	300	3.5	0.188	86	0.96	-20 ± 29	-2.08	810
		0.1M LiOH	300	3.5	0.188	86	0.80	-19 ± 28	-2.38	810
		0.1M NaOD	300	3.5	0.188	86	0.96	-11 ± 49	-1.15	810
		0.1M NaOH	300	3.5	0.188	86	0.61	-55 ± 53	-9.02	810
	2 mm Pd Rod[d]	0.1M LiOD	300	3.1	0.094	98	0.93	61 ± 26	6.56	740
		0.1M LiOH	300	3.1	0.094	98	0.78	40 ± 53	5.13	740
		0.1M NaOD	300	3.1	0.094	98	0.94	36 ± 40	3.83	740
		0.1M NaOH	300	3.1	0.094	98	0.62	-12 ± 38	-1.94	740
	1 mm Pd Rod[d]	0.1M LiOD	300	2.8	0.071	106	0.98	43 ± 64	4.39	670
		0.1M LiOH	300	2.8	0.071	106	0.83	-46 ± 64	-5.54	670
		0.1M NaOD	300	2.8	0.071	106	0.98	-4 ± 35	-0.41	670
		0.1M NaOH	300	2.8	0.071	106	0.62	-18 ± 60	-2.90	670
IHF[s]	2 mm Pd Rod[d]	0.1M LiOD	489	3.1	0.157	156	2.341	78 ± 77	3.35	231 (m)
		0.1M LiOD	490	3.1	0.157	156	2.380	27 ± 48	1.14	206 (m)
		0.1M LiOD	687	3.1	0.157	219	3.842	-1 ± 58	-0.03	187 (m)
		0.1M LiOD	876	3.1	0.157	279	5.188	-55 ± 101	-1.07	173 (m)
	Cast Pd[e]	0.1M LiOD	501	14	0.875	35	2.172	100 ± 40	4.61	236 (m)
		0.1M LiOD	502	14	0.875	36	2.219	47 ± 36	2.11	201 (m)
		0.1M LiOD	687	14	0.875	49	3.489	-31 ± 51	-0.90	187 (m)
		0.1M LiOD	876	14	0.875	62	4.863	-120 ± 86	-2.46	173 (m)
Isothermal	2 mm Rod[d][r]	0.1M LiOD	200	1.3	0.063	159	0.925[l]	-6.3 ± 6.0	-0.67%	238.87
	Cast Pd beads[f][r]	0.1M LiOD	250	5	0.5	50	0.985	37	3.75	7 (o)
		0.1M LiOD	150	5	0.5	30	0.415	11.1 ± 1.8	2.68	15 (o)
		0.1M LiOD	350	5	0.5	70	1.796	15.5 ± 4.5	0.86	7.8 (o)
		0.1M LiOD	100	5	0.5	20	0.214	8.4 ± 4.0	1.60	15 (o)
		0.1M LiOD	500	5	0.5	100	3.405	17.2	0.51	8.6 (o)
		0.1M LiOD	600	5	0.5	120	4.825	35.0 ± 7.03	0.73	270 (o)
		0.1M LiOD	200	5	0.5	40	0.675	9.4	1.39	8.1 (o)
		0.1M LiOD	400	5	0.5	80	2.311	23.7 ± 5.0	1.03	5.7 (o)
		0.1M LiOD	1000	5	0.5	200	12.314	79	0.64	4.8 (o)
		0.1M LiOD	800	5	0.5	160	8.140	41	0.50	4.1 (o)
		0.1M LiOD	1100	5	0.5	220	14.675	97	0.66	4.8 (o)

TABLE 1 - Calorimetry Results - PART 2

Calorimeter Type	Cathode Material	Electrolyte	i/mA	$\sim$ Surface Area /cm^2	$\sim$ Volume/cm^3	$\sim$i/mAcm^3	Mean input[(a)] Power/W	Excess Power /mW[(b)]	% Excess[(c)]	$\sim$ Charging time (hours)
Isothermal	Pt Foil[(g)(r)]	0.1M LiOD	500	12	0.6	42	3.593	33	0.92	
		0.1M LiOD	1000	12	0.6	83	13.078	105	0.81	
		0.1M LiOD	200	12	0.6	17	0.701	6.5 ± 2.3	0.92	
		0.1M LiOD	800	12	0.6	67	8.806	69	0.78	
		0.1M LiOD	400	12	0.6	33	2.489	9.2 ± 3.9	0.37	
	Nichrome Wire Heater[(h)]	0.1M LiOD	400				2.301	20	0.87	
		0.1M LiOD	800				9.490	63	0.67	
		0.1M LiOD	1000				15.084	114	0.76	
		0.1M LiOD	600				5.390	35	0.64	
		0.1M LiOD	500				3.736	21 ± 3.2	0.56	
	Melt Spun Pd[(i)(s)] Ribbons	0.1M LiOD	1000	74	0.35	14	8.991	128 ± 13	1.42	73.79
	Nichrome Wire Heater[(h)(q)]	0.1M LiOD	800				9.776	18.3 ± 3.2	0.19	
		0.1M LiOD	500				7.359	10.3	0.14	
		0.1M LiOD	1000				15.290	40.8 ± 13.3	0.27	
		0.1M LiOD	200				0.605	3.0	0.50	
		0.1M LiOD	600				9.132	-1.7	-0.02	
	2 mm Pd Rod[(j)(s)]	0.1M LiOD	200	1.3	0.066	152	1.091	12.1 ± 3.9	1.11	70 (p)
		0.1M LiOD	700	1.3	0.066	530	10.358	89.1 ± 8.4	0.86	253
	Pt Foil[(g)(s)]	0.1M LiOD	700	6.0	0.4	117	6.879	42 ± 15.2	0.62	
	Cast Pd[(k)(s)]	0.1M LiOD	850	28	1.48	30	8.974	100 ± 11	1.12	520

Notes for Table 1 - Calorimetry Results

a: Mean joule input power supplied to cell : see figure 2 caption. Values for IHF and isothermal calorimeters have been corrected for heat loss due to evaporation: see figure 1 caption.
b: Excess power = Measured cell output power - Calculated joule input power.
c: % excess = (excess power x100) ÷ mean joule input power.
d: Specpure (Johnson Matthey (JM)), drawn from sintered material.
e: Specially produced material supplied by JM:- Prepared from cast Pd stock which was argon arc melted into rod form using a gravity casting process. The rods were subsequently sliced and bent to decrease the loading time required (maximum distance from bulk to surface ∿ 1mm). The sample was cleaned using acetone, 10% HC and distilled water.
f: Pd Metal argon arc melted to form beads.
g: 125 μm thick (JM)
h: Glass clad (resistance ∿15Ω)
i: A variety of ribbons prepared (JM) by melt spinning of cast or sintered Pd. A proportion of the ribbons were heat treated (JM) for 20 minutes at 100°C under 10% H_2/N_2.
j: Type d) which was subsequently vacuum degassed at 1200°C, and loaded with deuterium at a pressure of 40 bar. The sample was cooled to liquid N_2 temperature prior to transferring to the calorimeter to minimise loss of D_2.
k: Specially produced material supplied by JM:- consisted of a sintered Pd bar which was sliced and bent to decrease the loading time required. (Maximum distance from bulk to surface ∿1 mm).
l: The value of the cell voltage, which was used in this calculation, contained a small contribution from the IR drop in the external leads which supplied current to the cells.
m: Total charging time = 797 hrs
n: Total charging time = 797 hrs
o: Total charging time = 355 hrs
p: Total charging time = 323 hrs
q: Calorimeter baseline power (power at zero cell current) increased by 36 mW over the period of the experiment.
r: D_2O from Harwell reference stock, contains 13 kBq/ml tritium.
s: D_2O from Aldrich Chemical Co., contains ∿15 Bq/ml tritium.

Cathode					Details of Electrolysis			Measured 5488 keV Gamma Yield: see note y		
Material	Mass(g)	Surface Area (cm^2)	Electrolyte see note w	Anode	Current (mA)	Typical Voltage	Duration (h)	γ sec s^{-1}	γ g^{-1} sec^{-1}	γ cm^{-2} sec^{-1}
Pd Foil	0.58	7.5	0.1M LiOH	Pt Foil	450	9	45	$(-4.9 \pm 7.43) \times 10^{-3}$	-0.008 ± 0.013	$(-6.5 \pm 9.9) \times 10^{-4}$
Pd Foil	0.74	9.5	0.1M LiOH	Pt Foil	510	9	164	-0.011 ± 0.004	-0.015 ± 0.005	$(-1.2 \pm 0.5) \times 10^{-3}$
Pd Sheet	7.7	12.9	0.1M LiOH *	Pt Foil	200	4.6	50	-0.017 ± 0.012	$(-2.2 \pm 1.6) \times 10^{-3}$	$(-1.3 \pm 0.9) \times 10^{-3}$
Pd Rod	3.1	2.3	0.1M LiOH	Au Foil	1000	26	17	0.008 ± 0.011	$(2.6 \pm 3.5) \times 10^{-3}$	$(3.5 \pm 4.8) \times 10^{-3}$
Ti Foil	0.089	2.0	"Jones" *	Au Foil	320	5	42	-0.022 ± 0.011	-0.25 ± 0.12	-0.011 ± 0.06
Ti Foil	2.2	32	"Jones"	Au Foil	1000	4	12	-0.015 ± 0.034	-0.007 ± 0.015	$(-0.5 \pm 1.1) \times 10^{-3}$
Ti Foil	2.2	32	"Jones"	Au Foil	1000	4	6	0.012 ± 0.007	$(5.5 \pm 3.2) \times 10^{-3}$	$(3.8 \pm 2.2) \times 10^{-4}$
Ti Granules	25		"Jones"	Au Foil	710	13	8	0.032 ± 0.036	$(1.3 \pm 1.4) \times 10^{-3}$	
Ti Granules	25		0.1M H_2SO_4	Au Foil	400	20	25	-0.019 ± 0.018	$(-7.6 \pm 7.2) \times 10^{-4}$	
Ti Granules	25		0.1M H_2SO_4	Au Foil	765	16	16	0.017 ± 0.022	$(6.8 \pm 8.3) \times 10^{-4}$	
UPt_3 Granules	42		0.1M LiOH	Pt Foil	300	31	166	$(3.1 \pm 6.0) \times 10^{-3}$	$(0.7 \pm 1.4) \times 10^{-4}$	

Notes for Table 2 - Measured Neutron and Gamma-Ray Emission Rates For Cold Fusion Electrolytic Cells

a: Cells provided by M. Fleischmann. Cathodes analysed for H, D after use - results H/D:0.01, 0.02 D/Pd:0.84, 0.72

b: Cathode wound into a tight spiral. Examined initially in the large n-detector, without shuttle, for 147 hrs with estimated detection limit 1n s^{-1} and a fu[illegible] 5 hr with detection limit 0.2 ns^{-1}. Surface of cathode then poisoned with S before further use

c: Cathode cleaned with emery paper after 300 hours

d: Cathode examined initially in the large n-detector, without shuttle, in 0.1M LiOD for 183 hrs; estimated detection limit 1ns^{-1}. Abraded with 400 grit SiC paper before use

e: Tubes from D storage system for Tokamak.

f: Foil vacuum degassed 1000°C before use

g: Foil dipped in Na_2S (conc soln) before use

h: 4 (1-2) mm thick/discs of different types of Pd (Johnson-Matthey) spot welded to Pd wires plus strained Pd Wire

i: Material heated to 900°C then quenched in water before use

j: Cathodes analysed for H, D after use-results: H/Pd: 0.02 D/Pd: 0.85

k: Cathodes analysed for H, D after use-results: H/Pd: 0.01 D/Pd: 0.88

l: Cathodes analysed for H, D after use-results: H/Pd: 0.02 D/Pd: 0.82

m: AuCN in Jones electrolyte replaced with $NaAuCl_4$

n: Current on for 36 hours then change 200/20mA every hour

o: Current on for 36 hours then change 300/30mA every 5 minutes

p: Current changed slowly over range shown during electrolysis period as anode disintegrated

q: Current on for 36 hours then cycle off for 10 hours and on for 2 hours for period of 270 hours. Then 5000s at 380mA cathodic and 4000s at 10mA anodic for rest of period.

r: Current cycled on/off every 2 hours. Neutron yield is for on cycle

s: Cells exchanged every 5 minutes by hand

t: These data were attained using different data acquisition system to drive shuttle and accumulate data, set up to look for neutron bursts - neutron burst results will be reported at a later date.

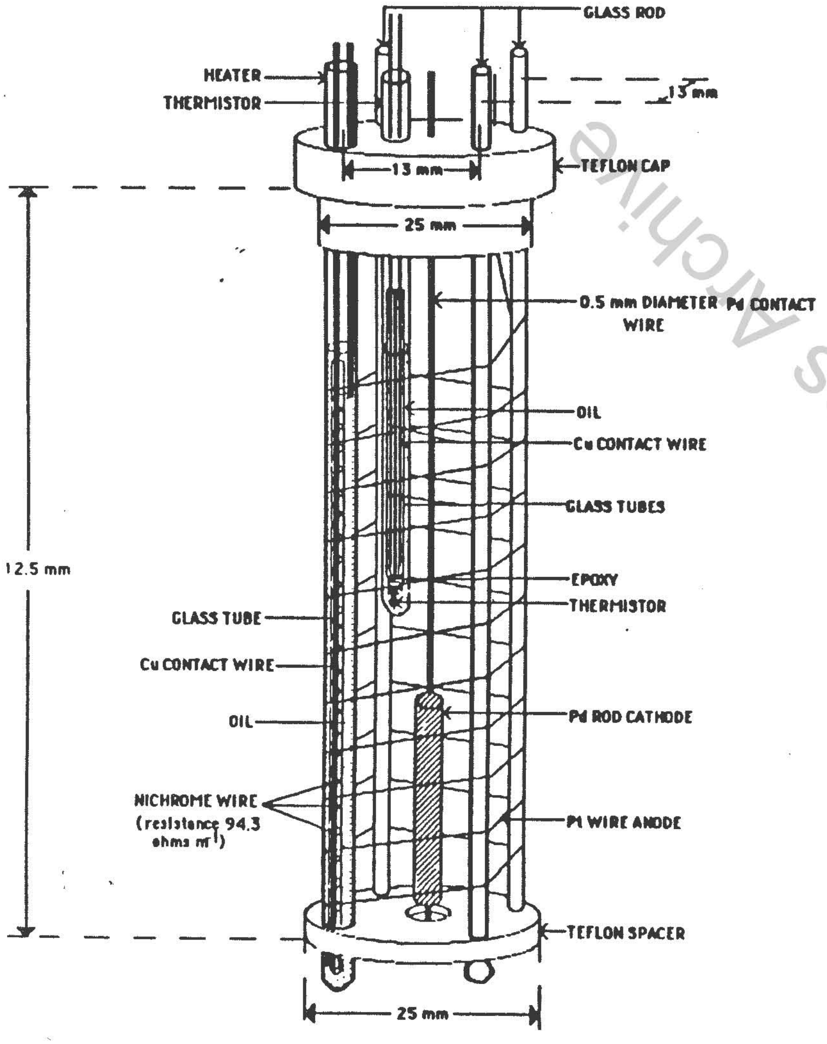
u: Melt-spun ribbon provided by Johnson-Matthey Technology Centre

v: 2-times arc remelted; electrolytically charged for 1 month in 0.1M LiOD then frozen in Liq.N_2, dipped in conc Na_2S soln and transferred to n-counting cell. Subsequently left charging in dual cavity detector together with 3 other arc remelted pellets removed from the isothermal calorimeter. No detected n-emission.

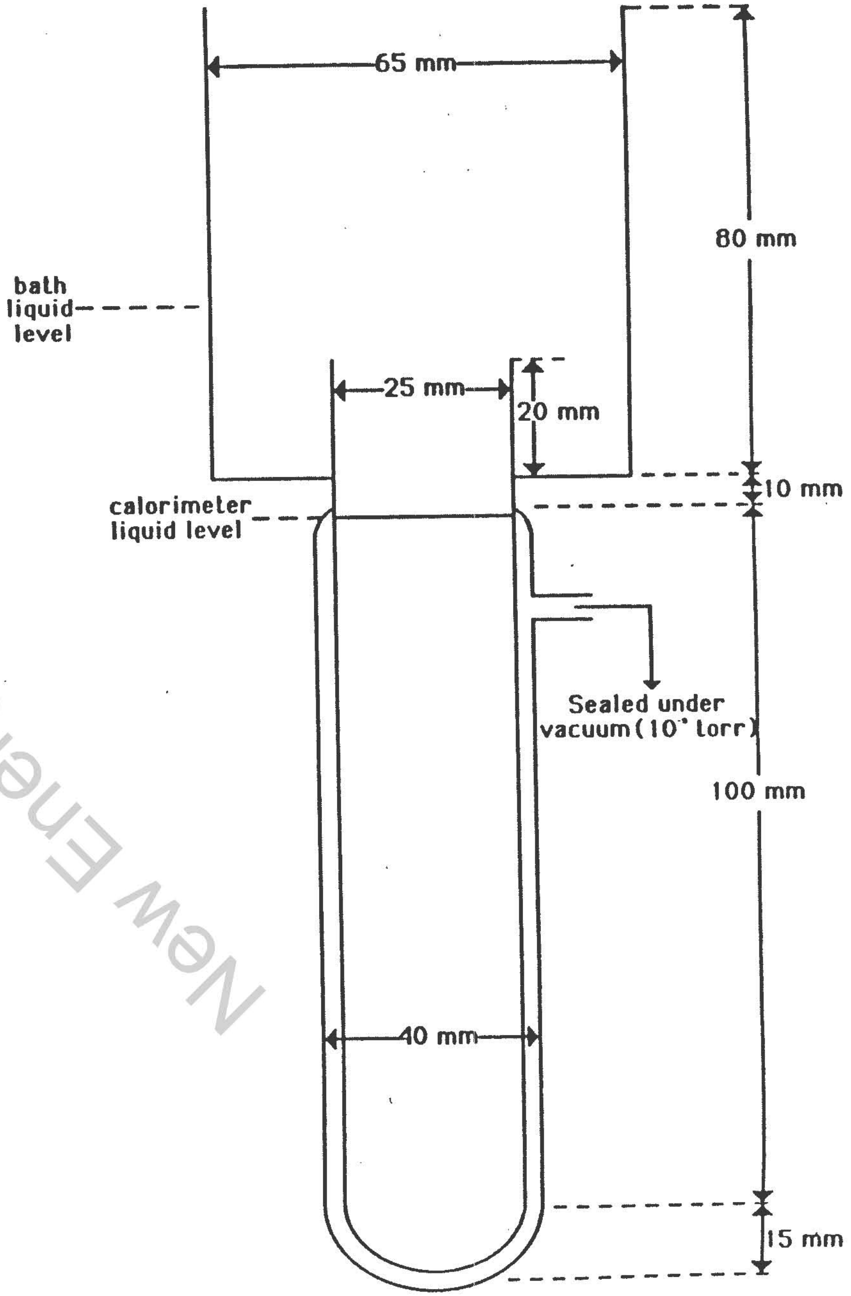
w: All electrolytes used for γ ray work were 50:50 H_2O:D_2O except * which were 41:59 H_2O:D_2O

x: The errors assigned vary somewhat because in an attempt (mostly in the earlier stages of the programme) to cover as wide a range of cell configurations as possible, pairs of unpowered+unpowered and powered+unpowered runs were not always carried out, and consequently allowance has to made for slight differences in overall cosmic-ray neutron detection efficiencies caused by slight differences between the two nominally identical cells.

y: For the present measurements, the system was calibrated with a set of standard gamma-ray sources and a $^{238}Pu/^{13}C$ $(\alpha, n\gamma)$ source emitting 6129 keV gamma-rays. The cells were positioned such that their cathodes were as close as possible to the detector crystal, and the detection efficiencies were calculated by integrating previously measured (27) point efficiency functions over the cathode volume. Peaks were searched for at 5488, 4977 and 4466 keV corresponding to the expected location of the full energy, single escape and double escape peaks using the method recommended in (28).

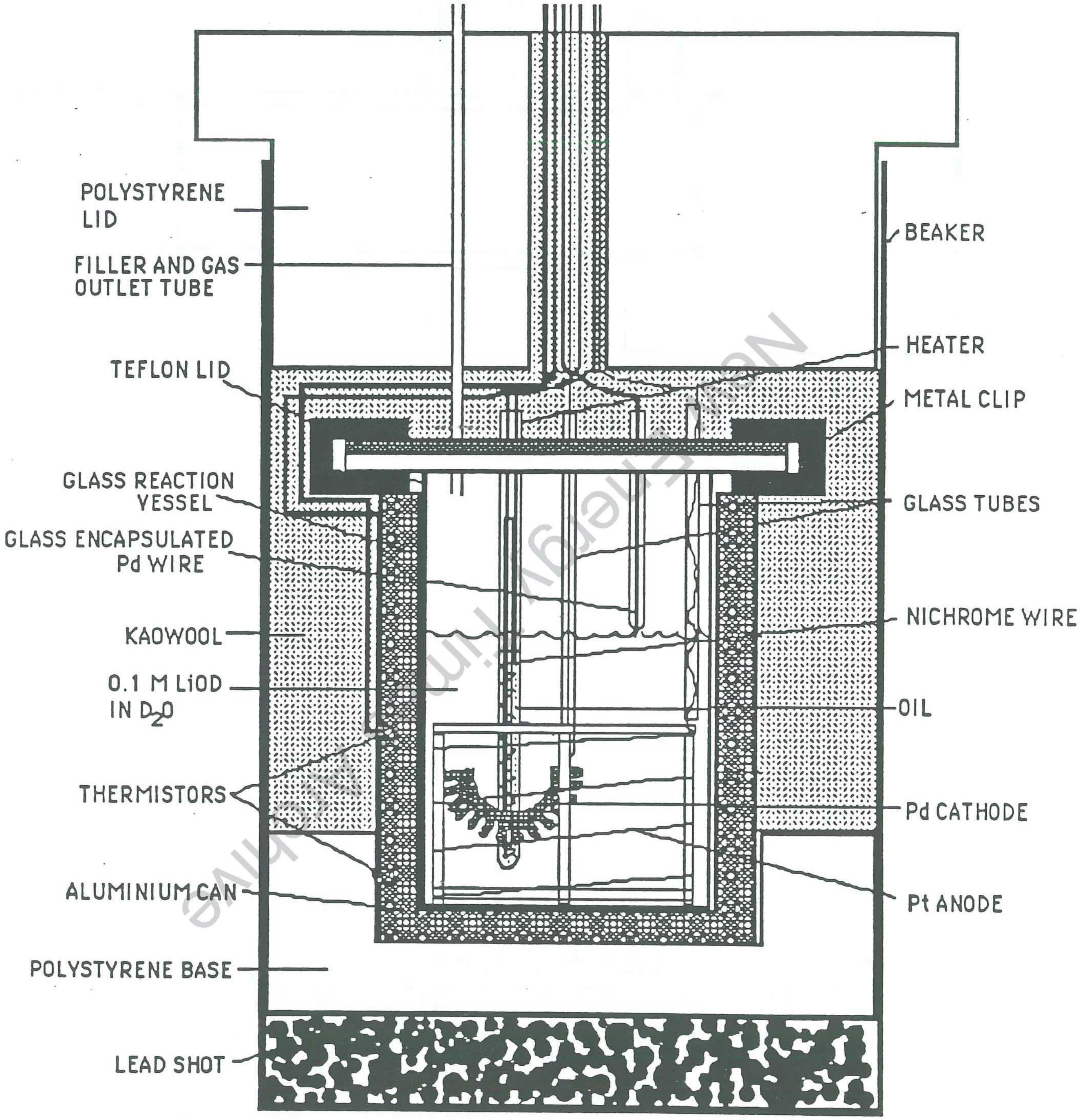


INNER COMPARTMENT



OUTER COMPARTMENT

(A)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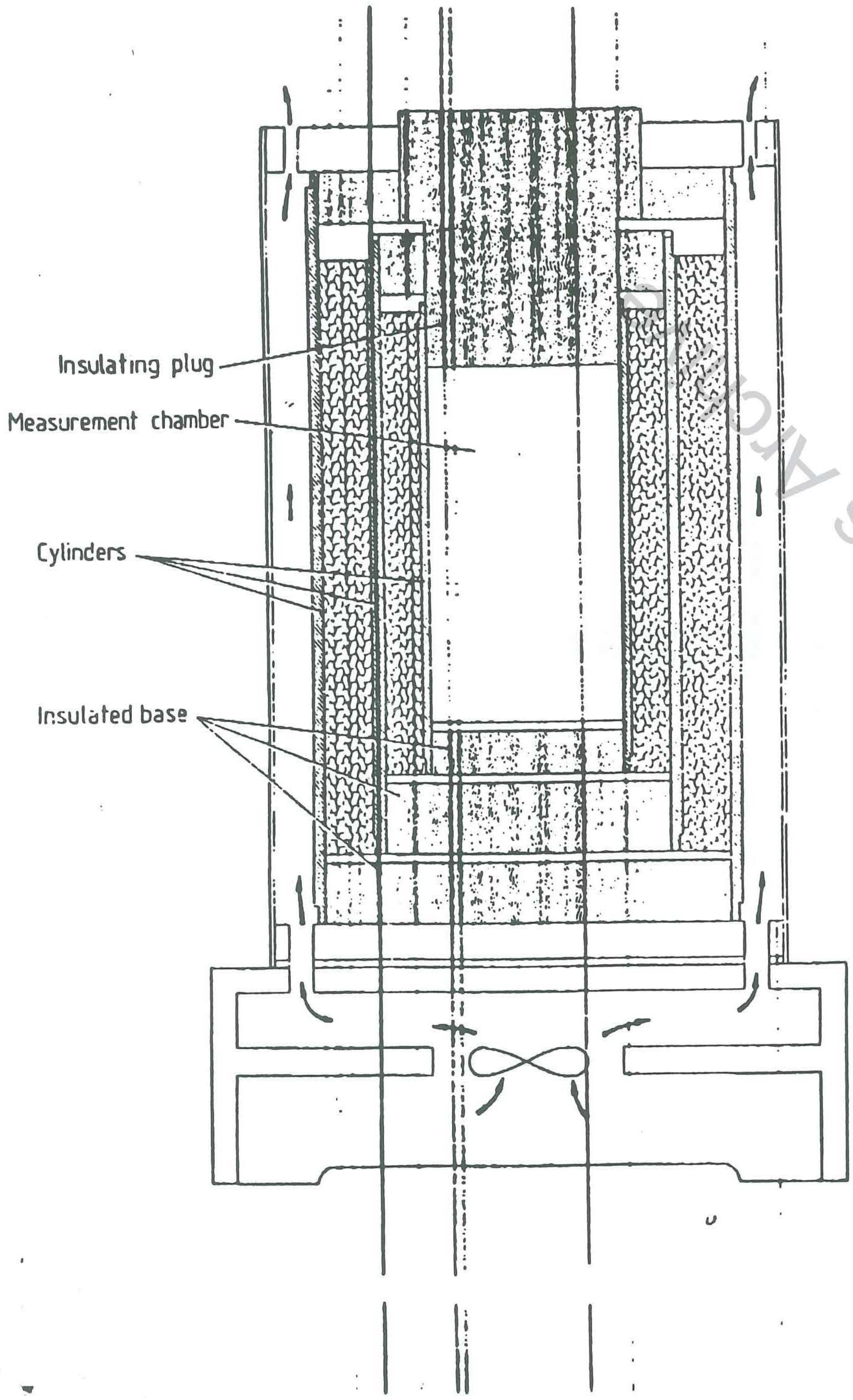
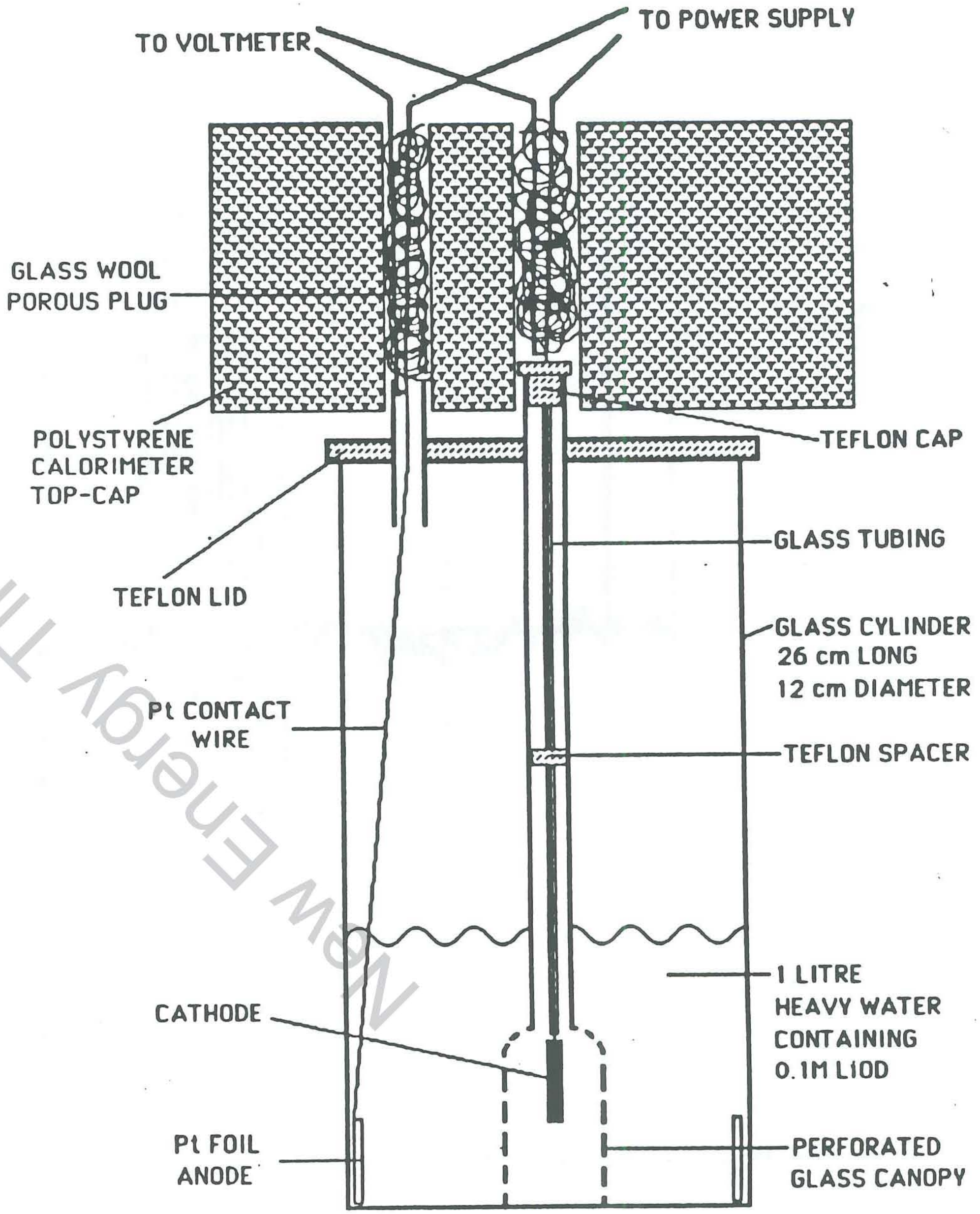
FILLER AND GAS OUTLET TUBE
TEFLON LID
GLASS REACTION VESSEL
GLASS ENCAPSULATED Pd WIRE
KAOWOOL
0.1 M LiOD IN D_2O
THERMISTORS
ALUMINIUM CAN
POLYSTYRENE BASE
LEAD SHOT
BEAKER
HEATER
METAL CLIP
GLASS TUBES
NICHROME WIRE
OIL
Pd CATHODE
Pt ANODE

(B)


Insulating plug
Measurement chamber
Cylinders
Insulated base


TO VOLTMETER
TO POWER SUPPLY
GLASS WOOL
POROUS PLUG
POLYSTYRENE
CALORIMETER
TOP-CAP
TEFLON CAP
GLASS TUBING
TEFLON LID
GLASS CYLINDER
26 cm LONG
12 cm DIAMETER
Pt CONTACT
WIRE
TEFLON SPACER
1 LITRE
HEAVY WATER
CONTAINING
0.1M LiOD
CATHODE
Pt FOIL
ANODE
PERFORATED
GLASS CANOPY

(C)

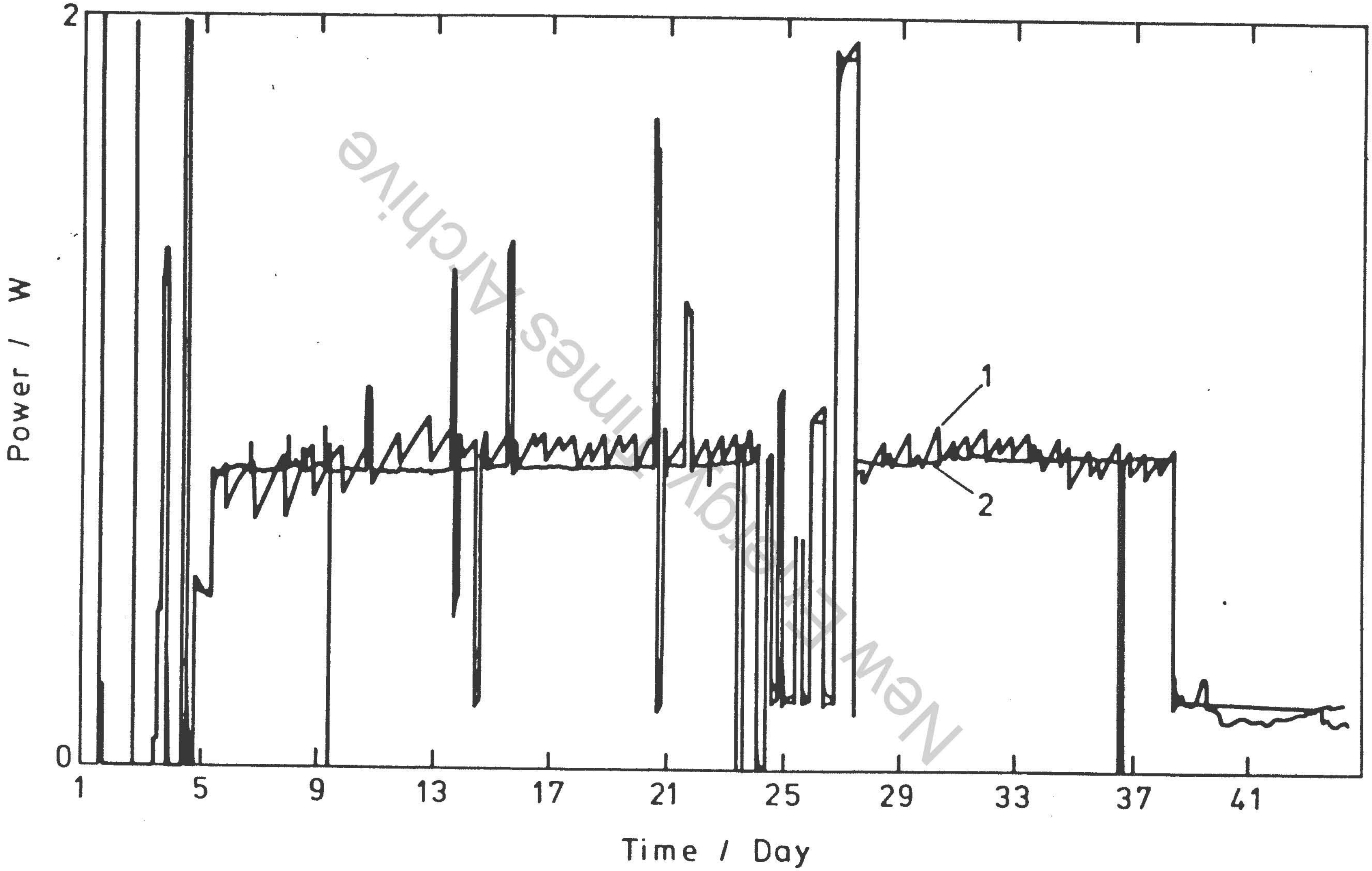


Fig 2 (a)

Fig 2(b)

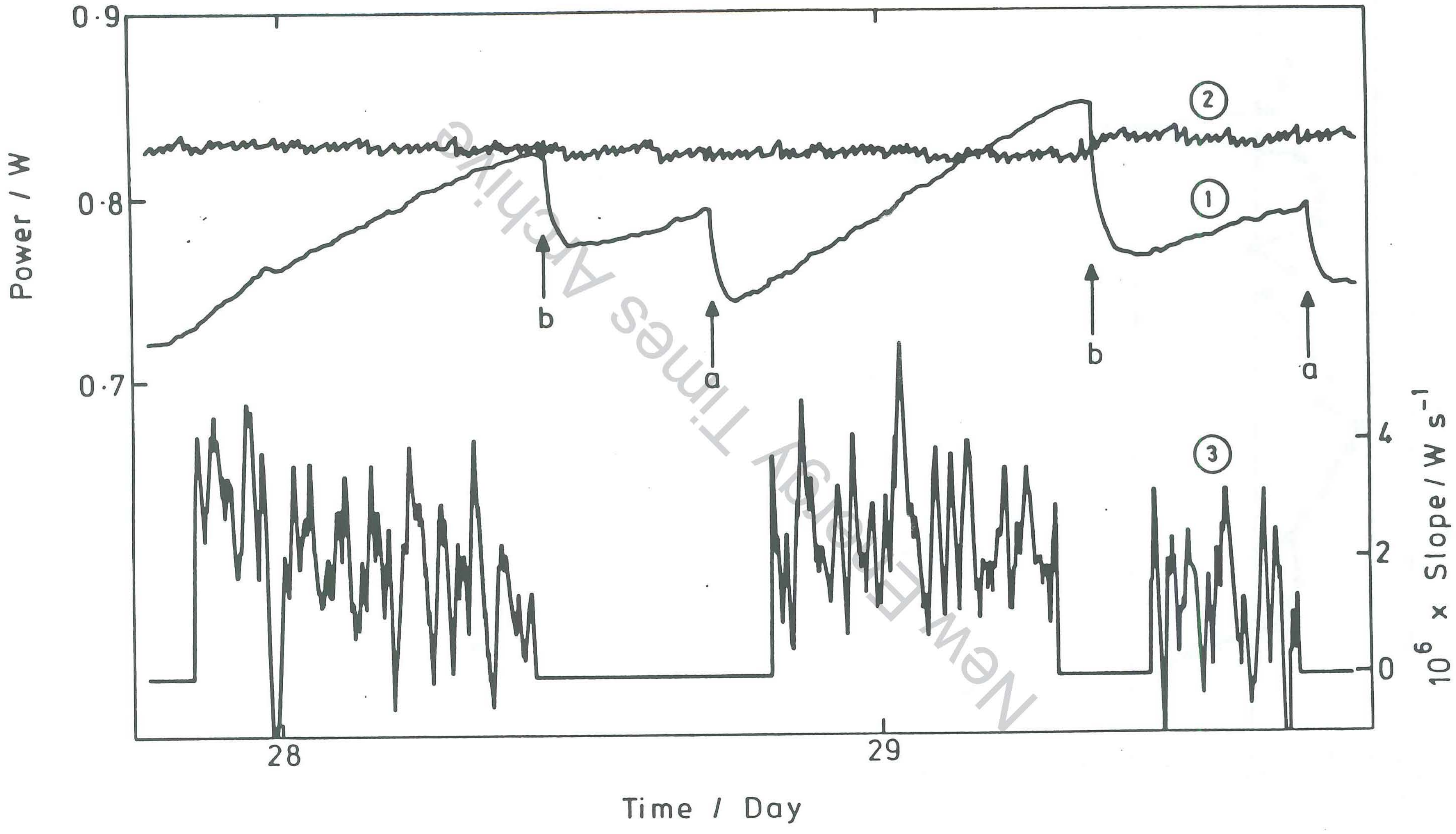
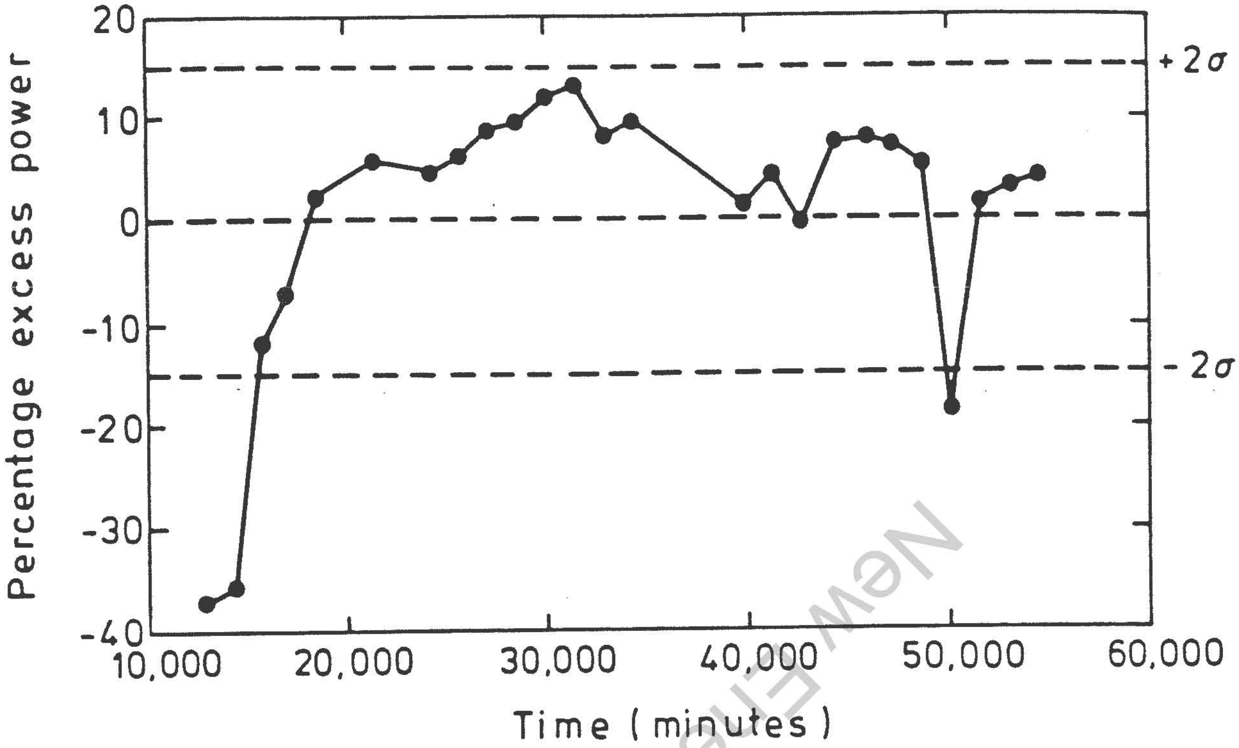


Fig 2c

2 mm Pd rod ; LiOH



2 mm Pd rod ; LiOD

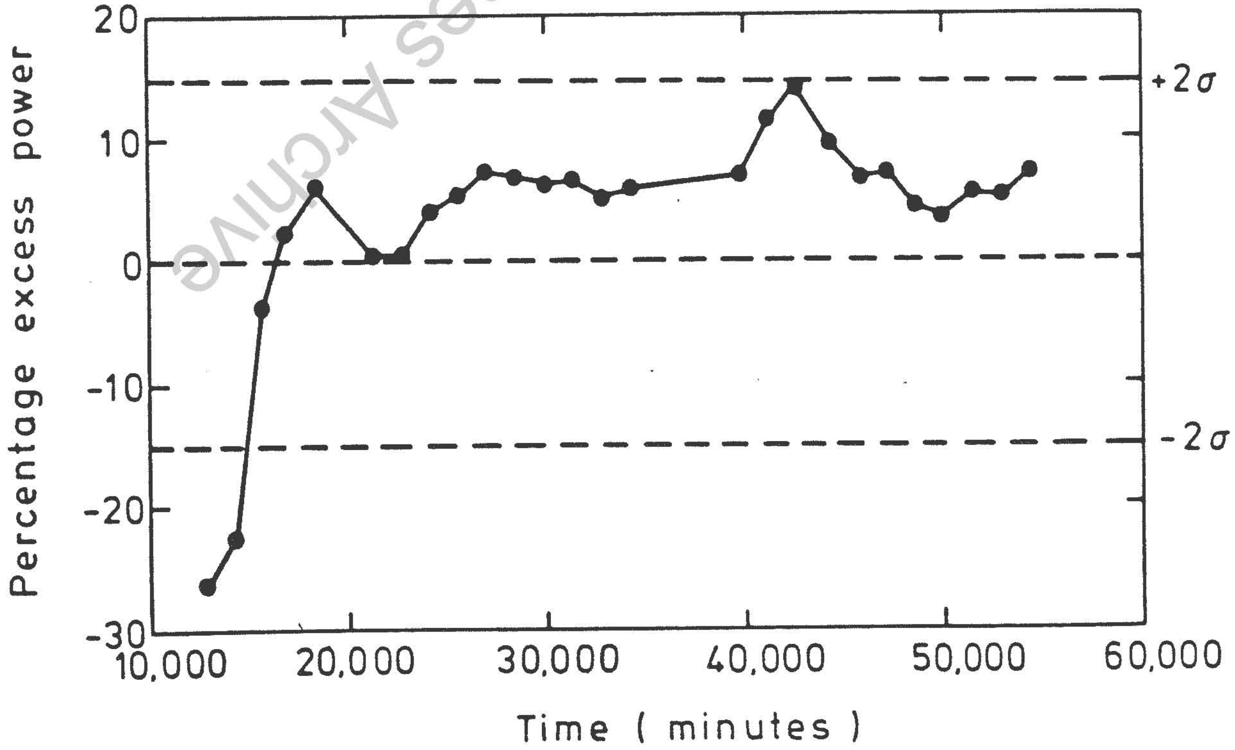
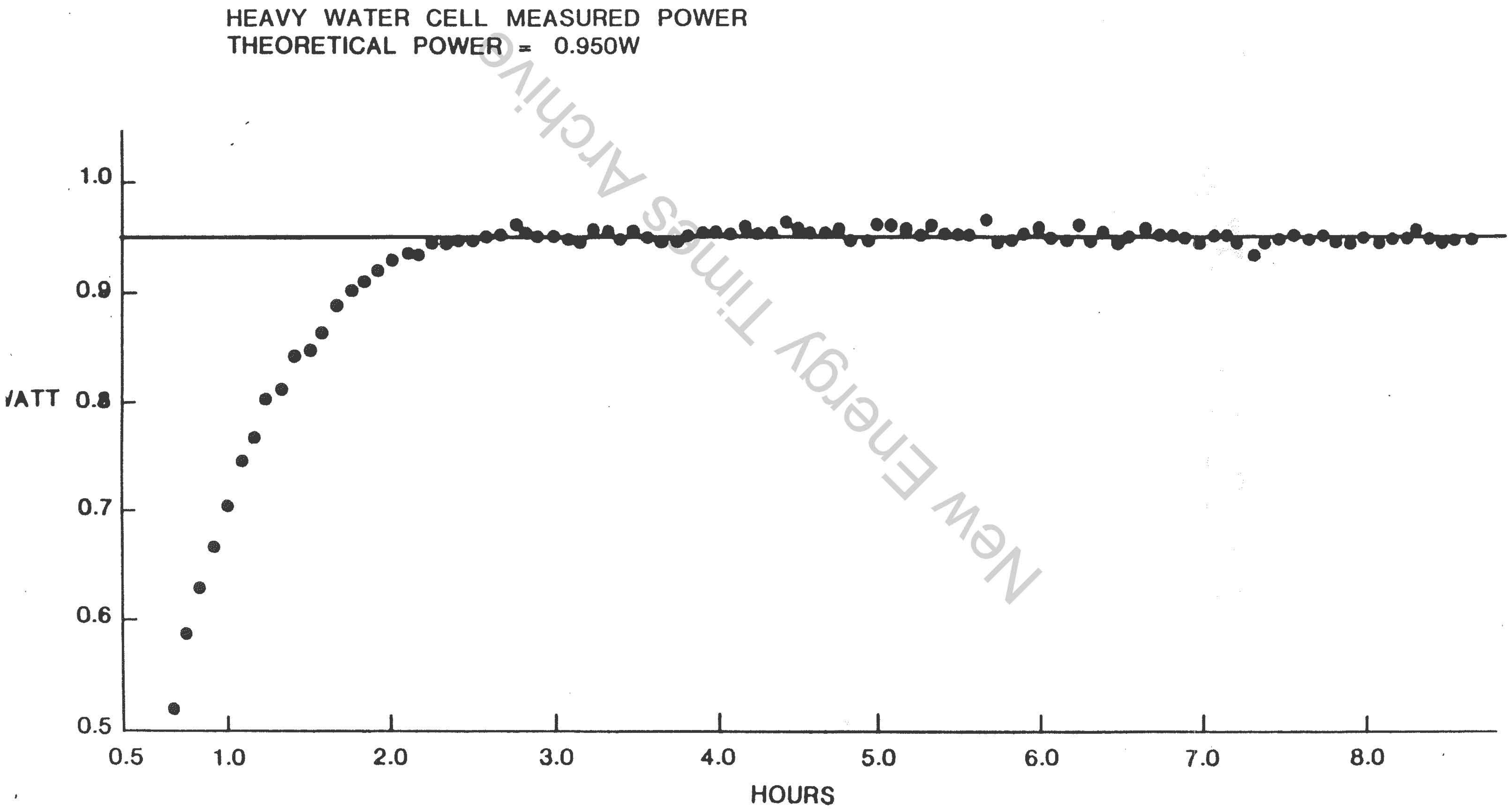
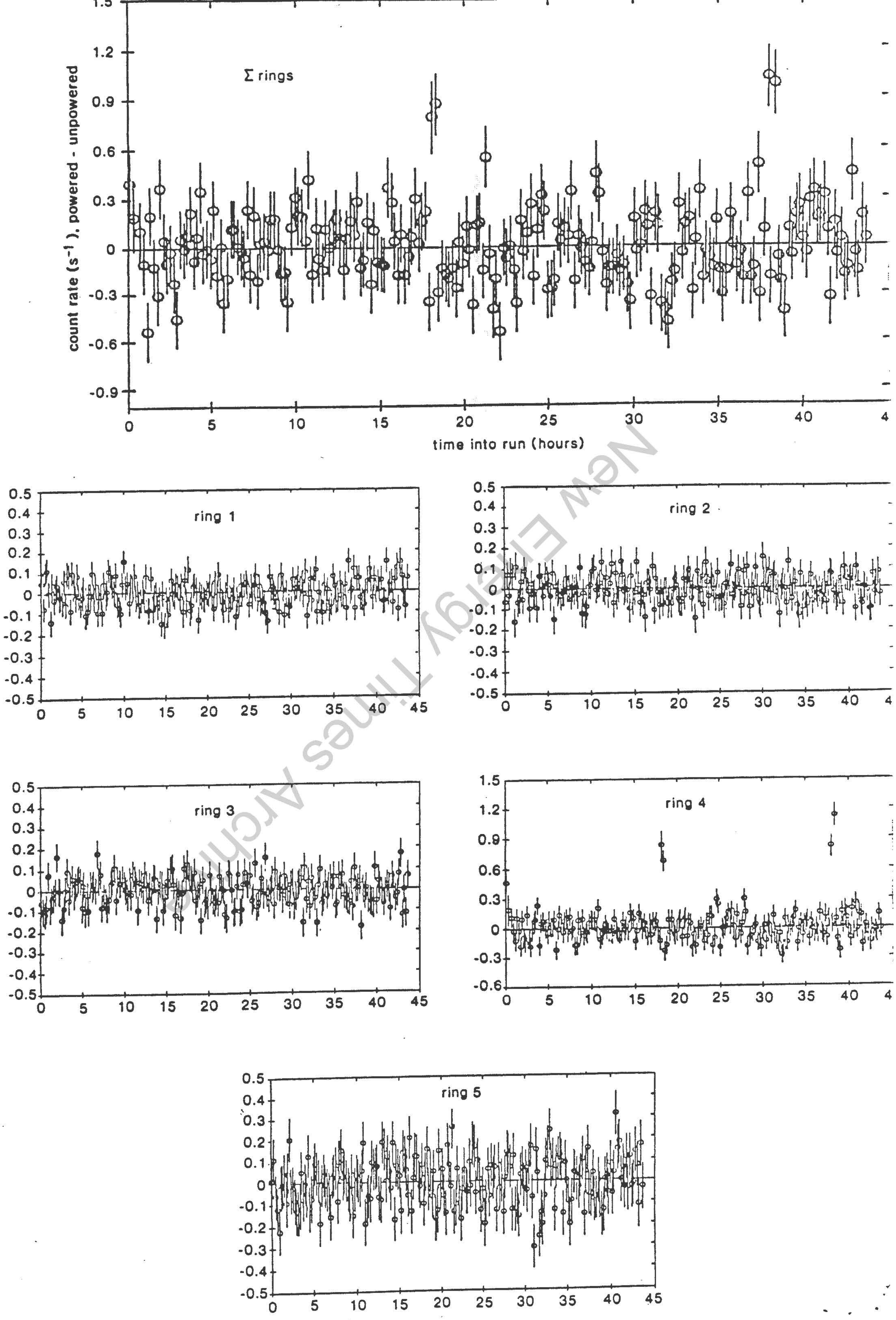
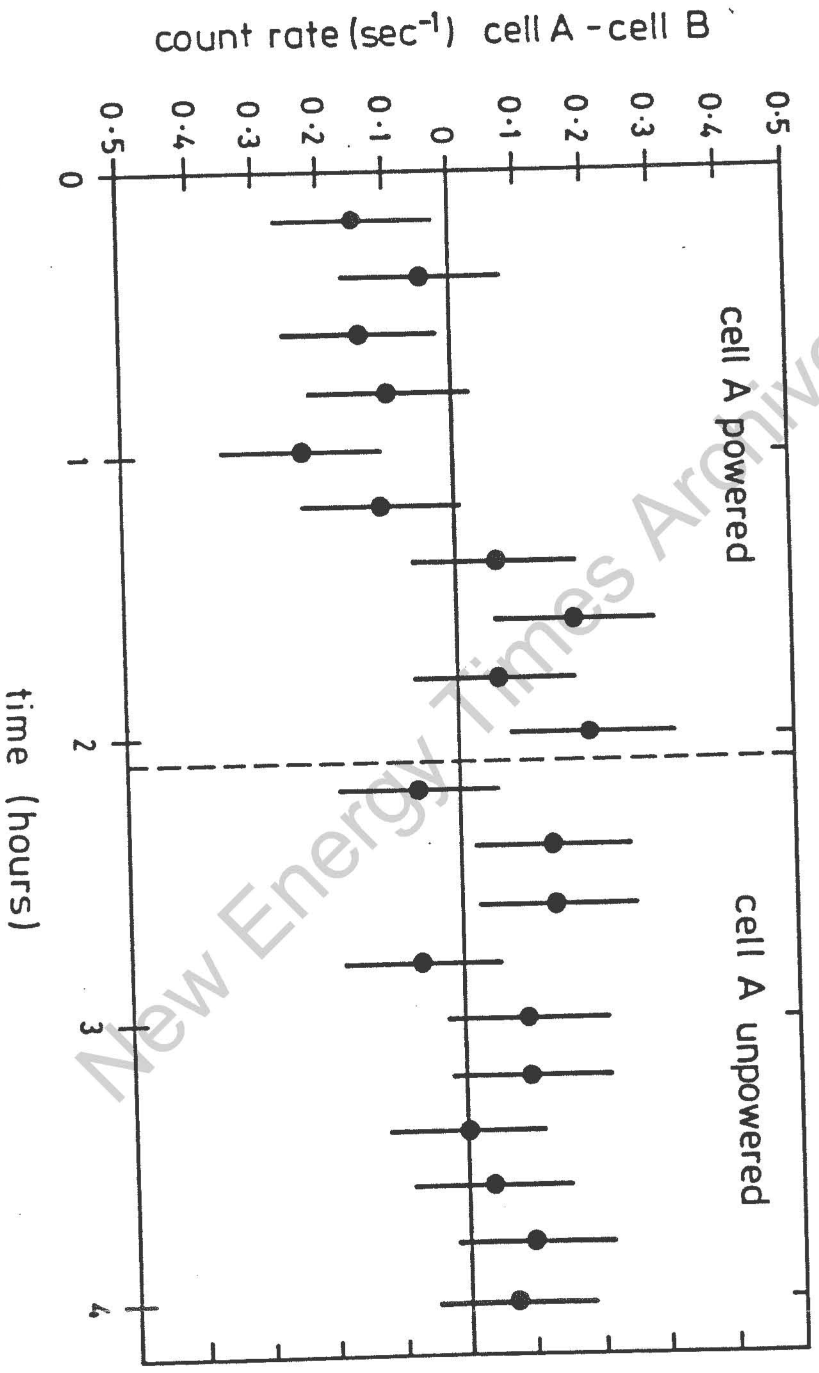


Fig 2(d)


HEAVY WATER CELL MEASURED POWER
THEORETICAL POWER = 0.950W
/ATT
1.0
0.9
0.8
0.7
0.6
0.5
0.5
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
HOURS


Σ rings
count rate (s⁻¹), powered - unpowered
1.5
1.2
0.9
0.6
0.3
0
-0.3
-0.6
-0.9
0
5
10
15
20
25
30
35
40
4
time into run (hours)
ring 1
ring 2
ring 3
ring 4
ring 5
0.5
0.4
0.3
0.2
0.1
-0.1
-0.2
-0.3
-0.4
-0.5
45
-0.6


count rate (sec⁻¹) cell A - cell B
0·5
0·4
0·3
0·2
0·1
0
0·1
0·2
0·3
0·4
0·5
0
1
2
3
4
time (hours)
cell A powered
cell A unpowered

DRAFT To Matthias for comment.

EXPERIMENTAL SEARCH FOR "COLD FUSION" IN THE DEUTERIUM-TITANIUM SYSTEM

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H J Milton, B A Powell, C Sadlor+, M Sene*, D R Sweetman, P Van Belle+,
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1. Introduction

The possibility of inducing nuclear fusion reactions at low temperatures in the solid state has recently been widely discussed (1). The evidence for such reactions occurring is based on two types of experiment. In the first type electrolysis of an aqueous solution using heavy water was used to load the surface of palladium and titanium with deuterium. Evidence of a low flux of 2.5 MeV neutrons was reported (2, 3). In the second type of experiment the surface of titanium was loaded by subjecting it to a high pressure of deuterium (4). Neutron emission was reported when the temperature of the titanium was cooled below room temperature and, with a separate sample, when the titanium was warmed up from 77K to room temperature.

We have attempted to repeat the second type of experiment using high pressure deuterium to load a titanium surface. In these experiments we have followed the procedure used by De Ninno et al as closely as possible. We have also varied their procedure by using a high temperature preparatory bake of the titanium in order to reduce the surface oxide layer. This procedure is well known to be necessary to get reproducible diffusion rates into bulk titanium. After preparation of the titanium the samples were taken to high efficiency neutron counters at JET and at Harwell. Counting was carried on for periods of many hours while the samples were cooled below ambient temperature and warmed up from 77K. In no cases were any neutrons detected above the background level. In the following sections we discuss the details of our techniques.

2. Preparation of the titanium samples

There appear to be two notable features of the deuterium loading technique described by De Ninno et al; it is carried out a high pressure and at relatively low temperature. The equilibrium pressure over deuterated titanium as a function of temperature and concentration has been given by Morton and Stark (5). Although deuterium diffuses through titanium quite rapidly at temperatures above 300°C, at lower temperatures it takes inconveniently long times to reach equilibrium conditions. An additional problem is that titanium forms a strong surface oxide coating and this coating can seriously impede the absorption of hydrogen isotopes. For this reason our apparatus has been designed so that it can be baked to high temperature, that it is capable of obtaining ultra high vacuum and that is is also capable of being operated at pressures of up to 50 bar. The system is shown schematically in fig 1. It is evacuated with a turbomolecular pump and the residual gas pressure is measured with an ion gauge and analysed with a quadrupole mass spectrometer. Joints were made with all metal seals. The deuterium gas comes from a cylinder which has a purity level > 99.9%. The main impurities are hydrogen (900ppm) and nitrogen (90 ppm). The gas inlet manifold consists of stainless steel pipe which goes through a liquid nitrogen cooled trap before entering the main system through valve 1. The gas pressure is measured by dial gauges on both the inlet system and the main system.

The titanium is prepared from commercially pure (99.5%) bar by milling under clean conditions without lubricant. The chips produced are typically 3 x 3 x 0.15mm. They are ultrasonically cleaned in Genklene and isopropyl alcohol, then weighed and put in the retort tube. The retort is 30 mm OD with 3 mm thick walls. After pumping the vacuum system down to typically < 10^{-6} mbar the retort is heated up to outgas titanium. A range of temperatures from 185°C to 670°C has been used for the different samples. The samples are then cooled down to near ambient temperature. The base pressure in the vacuum system is typically < 1×10^{-7} mbar at stage, with the main residual gas species being water. The pumping system is valved off using valve 3, and deuterium is introduced via valve 1. The pressure is raised quickly to some predetermined value and the gas inlet valve resealed. The pressure is noted as a function of time. In most cases the temperature of the titanium increases during exposure to the high pressure deuterium. The rate of change of pressure ie the absorption rate then increases due to the increase in the diffusion rate. After a given time at high pressure the retort tube containing the titanium is sealed off using valve 2 and transferred to one of the two high efficiency counters. The neutron emission rate has been measured over a range of conditions during which the samples were cooled to -196°C and warmed up to room temperature again.

2. Description of the neutron measurements carried out on a titanium cell

2.1 Three separate neutron counting systems have been used. The first is a single BF_3 counter mounted close to the titanium preparation tube. The counter is surrounded by a polythene cylinder wrapped in a thin sheet of cadmium. This system was calibrated with a 9.1×10^4 Bq ^{252}Cf source. It has an efficiency of 4×10^{-4} for neutrons emitted into a solid angle of 4π from the position of the titanium sample. The counter was connected to a ratemeter with a 30s time constant and used for routine monitoring of the titanium samples during preparation. It had a relatively high background rate varying from 1 to 3 counts s^{-1}. The titanium samples would thus have to emit between 2,500 and 7,500 neutrons s^{-1} to double this rate.

Two separate high efficiency counters were used to detect neutrons after sample preparation. The first system is normally in use at JET for neutron activation studies and was used for the majority of the samples investigated. It is described in detail in the next section. The second is the system set up at Harwell to investigate neutrons from electrolytic cells of the Fleischmann type. It is described in section 2.3.

2.2 The JET neutron detection system

For the present investigation use was made of two identical neutron detection systems which are used to measure the delayed neutron activity of samples of fissile material. The two counting systems are located in a shielded counting room, separated from the JET tokamak by a 3 meter thick concrete wall. As both counting systems are in routine use, their efficiency and response are well known (5) and the counter assemblies are well suited for the measurement of neutron emission from titanium samples. Each assembly consists of a large polythene filled vessel into which six ionisation counters (35 mm long and 25 mm in diameter) are set in a compact regular hexagonal arrangement to form an approximately 4π geometry to samples which are placed in its centre. As the counters are most sensitive to thermal neutrons polythene is used as a moderator. The sensitivity to neutrons originating outside the assembly is very low as those neutrons will first be thermalized by the outer layer of polythene, after which a cadmium blanket will stop them diffusing into the counters. The detection efficiency for neutrons originating from within the assembly, on the other hand, is very high and accurately known to be 10%, ie 1 in 10 neutrons produced within the assembly will be detected. The counters are standard ^{3}He ionisation counters (4 bar of ^{3}He and 2 bar of Krypton) and have been selected for matched sensitivity and gain. They operate at a bias voltage of 2.52kV and a gas multiplication of about 20. They are used in pulse-mode and each exhibits a 3% dead time at a count rate of 5 kHz. The output pulses are processed by a charge pre-amplifier discriminator unit which incorporate two separate leading edge discriminators to allow neutron events to be distinguished from events due to gamma radiation and other sources of noise. To monitor the detection systems over long periods, typically many hours, a computerised data-taking system was set up which performed the data collection in many batches of 40 seconds duration. At the start of each batch the data collection hardware was programmed to take 400(*24) samples during which the counts from each of the two discriminator outputs of each of the 12 individual counters were integrated over a period of 100ms and stored in local memory. After 40 seconds a program was triggered to read the memory, store its information on disk and start the next batch. To have the possibility for a comprehensive analysis of the data, the information stored for each event included: a) the absolute time of the event with 100 ms precision, b) a channel identifier specifying the counter and the discriminator of that counter which recorded the event and c) the number of counts that channel produced within the 100 ms integration period. During the experiments both assemblies were monitored this way; one contained the titanium sample while the other was used to monitor the background.

The computer program also performed a real time analysis which attempted to bring out, most sensitively, any granularity in the observed count rate which might be indicative of burst-like events like those claimed by De Ninno et al (4). Such bursts, when of moderate intensity, would be detected properly. Very intence bursts of neutrons could paralyse the counters but such occurrences cannot escape detection. With a burst, intense enough to paralyse one counter, there is a near to absolute certainty that the remaining five counters in the assembly also register counts, or possibly paralyse. However, in that case, the lower and upper leading edge discriminators of each of the six counters would fire at least once and, more importantly, on all six counters simultaneously, ie within 100ms. Such an event would then be detected as a six-fold coincidence. Given that the average count rate is low (approximately 0.0035 counts/s), six-fold coincidences are extremely unlikely within a 100 ms period. Running both assemblies under normal conditions (ie no titanium sample present) confirmed that single, double and triple coincidences follow a predictable pattern which is easily derived from Poisson statistics assuming a constant background. Four fold, five fold and six fold coincidences, although monitored, are too unlikely to be seen at all with any statistical significance.

The capabilities of the detection system may therefore be summarised as follows:

a) absolutely calibrated detectors with a well known behaviour and a high neutron detection efficiency of 1 in 10 neutrons produced within the assembly
b) noise discrimination
c) coincidence detection, which is particularly sensitive to any non-statistical fluctuation in the background (eg neutron bursts)
d) complete paralysis of all detectors cannot go undetected.

2.3 Harwell Dual Cavity ^{3}He Detector

This detector was specifically constructed to provide a reasonable volume for continuously monitoring a number of electrolytic recent measurements at Harwell attempting to reproduce the cold fusion results of Fleischmann and Pons (2). The detector, shown schematically in figure 2, consists of two cavities each 38cm x 42cm x 60cm deep and each furnished with 16 2.5cm diameter, 35cm active length ^3He proportional counters filled to 4 bar with ^3He. The counters are grouped into banks of 8, there being 4 banks in all as numbered in figure 2. The counters are double bagged and sealed in polythene sheeting with silica gel dessicators. Behind the detectors are 40mm of polythene moderater and 12mm of Cd sheet. The base of the cavities is also lined with 1mm of Cd on top of the concrete laboratory floor. The cavities are covered with 1mm of Cd sandwiched between two 10mm thick layers of polythene. The top and all four sides of the detector are shielded with 150mm thickness of interlocking borated resin blocks. The same thickness of borated resin also divides the two cavities and both cavities are continuously vented through pipes connected to extractor fans.

Signals from each of the 4 banks of detectors, which operate at a voltage of 1560V, are shaped and amplified by Harwell type 0058 and 2151 preamplifiers and main amplifiers. Outputs from the amplifiers are passed to Harwell type 2170 single channel analysers with gates set around the thermal peaks in the pulse height spectrum from the counters. Accepted events are counted along with clock pulses from a crystal oscillator by a LeCroy type 2551 CAMAC scaler which is read at fixed intervals by a PDP II/45 computer.

For the present measurements, vessels containing the Ti chippings were surrounded by expanded polystyrene for thermal insulation and a third polythene sheeting seal was provided as an extra barrier between any condensation and the counters.

Under normal operation the background rate in each bank of counters lay in the range 0.05 to 0.2 counts per second with correlated changes in the rate in all four banks consistent with changes in the operational status of nearby neutron producing accelerators and reactors. Unexplained drifts in the count rate in one bank uncorrelated with the others have been observed (see for example bank 1 in figure 4) with time constants of the order of many hours. Such drifts can easily be distinguished from genuine neutron emission which would give correlated signals in the 2 banks viewing the cavity containing the source with any correlated rise in the other 2 banks being consistent with the known cross talk between the cavities.

The neutron detection efficiency of the detector was determined using a calibrated Am/B source, which has a neutron energy spectrum with a mean energy of 2.7 MeV, positioned by or in place of the titanium sample tube. The measured efficiencies for neutrons emitted from the base and the top of the column of Ti chippings in the pressure vessel in cavity B are given in Table I. These efficiencies together with the stability of the detector banks and the requirement for correlated rises in both counter banks in one cavity indicated a sensitivity of the detector of < 5 neutrons per second.

TABLE I

COUNTER	MEASUREMENT 1		MEASUREMENT 2	
BANK	TOP	BOTTOM	TOP	BOTTOM
1	(9.92+/-.38)E-4	(9.64+/-.37)E-4	(9.59+/-.30)E-4	(1.01+/-.03)E-3
2	(1.02+/-.04)E-3	(9.44+/-.37)E-4	(9.61+/-.30)E-4	(1.08+/-.03(E-3
3	((8.26+/-.11)E-3	(8.73+/-.14)E-3	(7.95+/-.40)E-3	(8.79+/-.40)E-3
4	(8.43+/-.11)E-3	(8.68+/-.11)E-3	(1.02+/-.10)E-2	(9.17+/-.40)E-3

3. Results

A summary of the preparation of the different samples is given in Table II. The different samples were exposed to deuterium over a range of temperature from 20°C to 125°C and pressures from 2 to 40bar. The preparatory baking temperature was also varied from 185°C to 675°C. In general when the samples are exposed to the deuterium in a sealed off system the pressure p drops as the deuterium is absorbed into the lattice. The rate dp/dt depends on the sample temperature, due to the change of diffusion coefficient with temperature. At room temperature the initial dp/dt is $\sim$ bar s^{-1} while at an initial temperature of 125°C it is < 1 bar s^{-1}. As the reaction is exothermic with a heat of solution of 12 kcals/mole the sample heats up as the deuterium is absorbed. At higher temperatures where the rate of absorption is more rapid the temperature rise is higher. The increase in sample temperature varies from $\Delta T = 10°C$ with the sample at 20°C to $\Delta T=290°C$ with the sample at initially at 125°C. In one case, sample 4, where the initial bake was 185°C both the absorption rate and the temperature rise were undetectable. This was attributed to the presence of an oxide layer which had not been removed by the low temperature bake. The samples prepared by heating to the higher baking temperature had a hydrogen absorption rate and temperature rise which behaved reproducibly.

In the first few experiments an attempt was made to reproduce the conditions reported by De Ninno et al (4) and to detect the relatively high neutron flux observed when the titanium samples were warmed from 77K to room temperature. The samples were loaded at high pressure and temperatures in the range 300-340K. They were then cooled to 77K and evacuated using the turbomolecular pump. No significant amount of gas was released at this stage. The valve 2 to the retort was then closed and the retort transferred to the high efficiency counter in a dewar. The retort was removed from the dewar and allowed to warm up in the counter. This typically took a period of 2 to 4 hours during which time the neutron rate was monitored both in the counter cavity in which the retort was contained and in the similar cavity without the retort (cf sections 2.2 and 2.3). Typical results are shown in fig 3 and 4. No neutrons above background were observed in any case. In the case of the JET counter with a background counting rate of ∿ 0.2 counts s^{-1} and an efficiency of 10% an increase of 0.002 counts s^{-1} could have been detected, corresponding to a total neutron production rate of 0.02 counts/sec. The 5000 neutrons/sec reported by De Ninno et al would have been detected unambiguously if such emission levels had occurred.

It has been reported that in the Frascati experiment the titanium sample was baked to 200°C (4). This is not the conventional procedure for loading hydrogen isotopes in titanium as oxide layers tend to impede the rate of diffusion. One sample was prepared in this way in case such a procedure was important for some unsuspected reason: however, in this case no evidence of deuterium absorption was observed ie no fall in deuterium pressure occurred nor was there any rise in the titanium temperature during exposure to the high pressure deuterium. No neutron flux above background level was detected when the samples were heated from 77 to 300 K. In the subsequent experiments a high temperature bake was used in order to remove the surface layer of oxygen and obtain reproducible absorption. In these cases, the samples were left at ambient temperatures and at loading pressure while they were sealed off and transferred to the high efficiency counters. They were then cooled and allowed to warm up again in situ in the counter cavity. In some cases they were cooled to ∿ 180 K using solid CO_2 and in other cases to 77K using liquid nitrogen. In a number of cases the same titanium samples were cooled and allowed to warm up again a number of times in succession. Two examples of the neutron counting rate as a function of time during the cooling and heating cycle are shown in figs 5 and 6. In no case was a significant neutron flux above background detected.

In all the runs up to this point the loading temperature was kept ∿ 300K. This led to rather low average deuterium concentrations in the titanium ∿ 0.1-0.2 D/Ti due to the low diffusion rates. However the concentration profile of deuterium in the solid is expected to be peaked at the surface as discussed in section 4. In the last two experiments the titanium chippings were deliberately heated to a higher temperature for loading. This results in a much larger quantity of deuterium absorbed and a consequently higher temperature excursion due to the exothermic reaction energy. In these cases the average deuterium concentration was ∿ 2.0/Ti. The concentration would be expected to be approximately uniform throughout the volume of the titanium in this case. No neutrons above the background rate were observed when the titanium samples were cooled or heated.

4. Discussion

Electrochemical charging and high pressure low temperature gas, are in many ways similar approaches to inducing a high deuterium concentration in a metal surface. Both have high incident flux rates, and since they are carried out near ambient temperature the rate of diffusion into the bulk is low. The diffusion coefficient for deuterium in titanium can be written (7)

$$D = 0.013 \exp(-12400/RT)$$

where Q = 12,400 kcals/mole, is the activation energy for diffusion and T is the absolute temperature. Although these data have been measured at temperatures above 770K it can be extrapolated to lower temperatures with reasonable confidence, obtaining a value of 2×10^{-11} cm^{2}s^{-1} at 300K. The characteristic diffusion length calculated on the basis of a one dimensional model is given approximately by $(4D\tau)^{1/2}$ where τ is the time for diffusion (6). Considering a loading time of 10^4 secs the diffusion depth will be $\simeq$ 9μm. This is small compared to the typical sample thickness of 150μm and so only the surface of the sample will be loaded. Thus the surface concentration will be much higher than the average concentration quoted in samples 1 to 8 tested in Table I. Taking into account diffusion from both sides the concentration in the loaded layer will be $\sim$ 1.3 D/Ti ie not markedly below the concentration in samples 9 and 10.

During our attempts to produce neutrons from cold fusion with the ten samples listed in Table I we have not seen any significant evidence of neutron production. The upper limit of neutron emission, if present at all is not higher than 0.02 neutrons s^{-1}. This is approximately 2000 times more sensitive than detectors used by De Ninno et al.

One possible explanation of the observations of De Ninno and other reports of cold fusion is that it is due to random and unpredictable fluctuations in the ionisation counters used to detect neutrons. Such fluctuations have been observed in all our counting systems, at Culham JET and Harwell. In all cases the apparent signals have been shown to be due to counter misbehaviour, as they usually occur only in one counter and continue even when the titanium sample is removed. In one case in JET the counting rate increased by a factor of 100 and remained high for many hours. The reason for this counter behaviour is still unexplained. It is particularly difficult to detect if only one counter is being used. If a number of independent counters are used the errant counter can be detected and its output rejected.

5. Conclusion

Ten separate titanium samples have been loaded with deuterium under high pressure in a way similar to that reported by other investigators (4). A number of variations in the procedure including a range of loading temperatures and pressures have been used. The prepared samples have then been transferred to high efficiency neutrons counters and cycled in temperature. In no case has any evidence for neutron production been observed. In the case of our highest efficiency counter the neutron production rate, if present at all, was less than 0.02 counts s^{-1}. This is 3 orders of magnitude lower than the rates of neutron emission claimed to have been observed by other groups.

It is of course quite possible that we have not found the correct preparation procedure of loading titanium. There are a large number of possibly important parameters and it has not been possible to explore all combinations. It is evident from other reports that the statistical probability of observing neutrons is low. It seems likely that if neutron emission does occur then the preparation of the samples is critical. It is thus important that more emphasis is placed on the careful preparation and documentation of procedures in the reports from successful experiments.

Our experience of making measurements of low fluxes of neutrons has indicated that proportional counters of both the BF_3 and ^3He type are subject to random and unpredictable fluctuations in count rate. These fluctuations can in some cases exceed the average background count by two orders of magnitude. Thus clearly a number of independent counters are necessary to confirm that neutrons are really present. We suggest that in a number of reported cases where only single, low efficiency counters have been used that these random fluctuations may have been mistaken for neutrons.

Figure Captions

Figure 1. Schematic diagram of apparatus used to load titanium with deuterium.

Figure 2 Schematic view from above of the Harwell neutron detector showing two cavities each with 2 banks of 8 ^{3}He detectors.

Figure 3 Neutron counting rate in the JET counter during the warm up of titanium from 77 to 300K. Sample No 1.

Figure 4 Neutron counting rate in the Harwell counter during the warm up of titanium from 77 to 300K. Sample No 2. The upper 4 plots show the mean count rate in each of the 4 counter banks. Data was collected in 10 second intervals but have been summed into 10 minutes bins. The lower plot shows the temperature of the vessel as measured by a K-type thermocouple in contact with the outside of the vessel.

Figure 5 Neutron counting rate in the JET counter during temperature cycling from 300 to 180K. Sample No 5.

Figure 6 Neutron counting rate in the Harwell counter during temperature cycling from 300 to 180K. Sample No 6. The conditions are the same as for fig 4.

References

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(2) M Fleischmann and S Pons, J of Electroanalytical Chemistry, 261 (1989) 301

(3) S E Jones, E P Palmer, J B Czirr, D L Deglaur, G L Jensen, J M Thorne, S F Taylor and J Rafelski, Nature 338 (1989) 737

(4) A De Ninno, A Frattolillo, G Lollabatista, L Martinis, M Martone, L Mori, S Podda and F Scaramuzzi, submitted to Europhysics Letters, April 1989

(5) J R Morton and D S Stork, Trans of the Faraday Soc, 56 (1960) 351

(6) JET neutron counter

(7) R J Wasilewski and G L Kehl, Metallurgia (1954) 225

(8) H S Carslaw and J C Jaeger. Conduction of Heat in Solids, 2nd Edition, Oxford University Press, Oxford (1959)

Run No	Date	Weight of Ti	Bake Temp	Nominal Loading Temp	Loading Pressure	VΔP	D/Ti	Neutron Counter	Comment
1	30/4-2/5	26.9	470	33-64 64	36.7	1.77	0.28	JET	Transfer at 77K. Warmed in counter
2	3-4/5	26.2	450	35-66	2.0	1.0	0.16	AERE	Transfer at 77K. Warmed in counter
3	3-4/5	26.9	-	20	34.0			JET	Transfer at 77K. Warmed in counter
4	8-9/5	30.3	185	30	40	0	0	JET	Transfer at 77K. Warmed in counter
5	10-12/5 12-15/5	35.5	665	20	17.0	2.6	0.31	Culham JET	Cooled and warmed again at Culham. transferred at ambient. Cooled in LN_2 at JET
6	15/5	35.0	675	23	18.4	1.17	0.14	AERE	Transfer to AERE at ambient. Cooled to -90°C & warmed again.
7	16/5	35.1	675	22.5	16.3	1.71	0.20	JET	Transfer at ambient. Cooled to 77K & warmed again
8	17/5	25	660	22	16.5	1.17	0.2	Culham	Cooled to 193K in situ & rewarmed to ambient
9	19/5	25	670	125	37.3	12.3	1.97	JET	Transfer at ambient. Cooled to 77K & warmed again.
10	26/5	35?	680	80	43	13.0	2.04	Culham	Cooled to 77K and warmed again

Vacuum / High Presure System for Loading Titanium with Deuterium

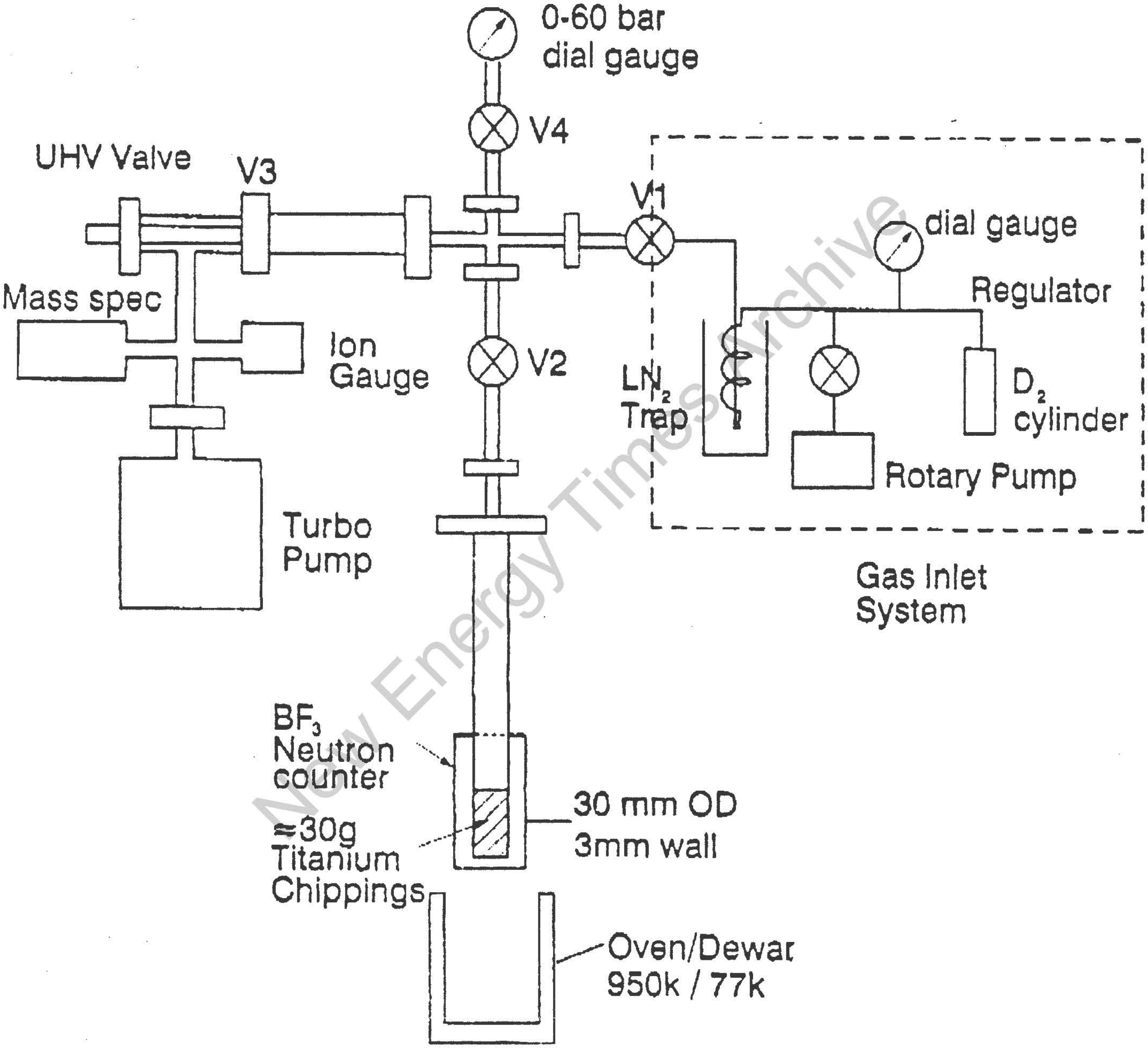

FIG 1

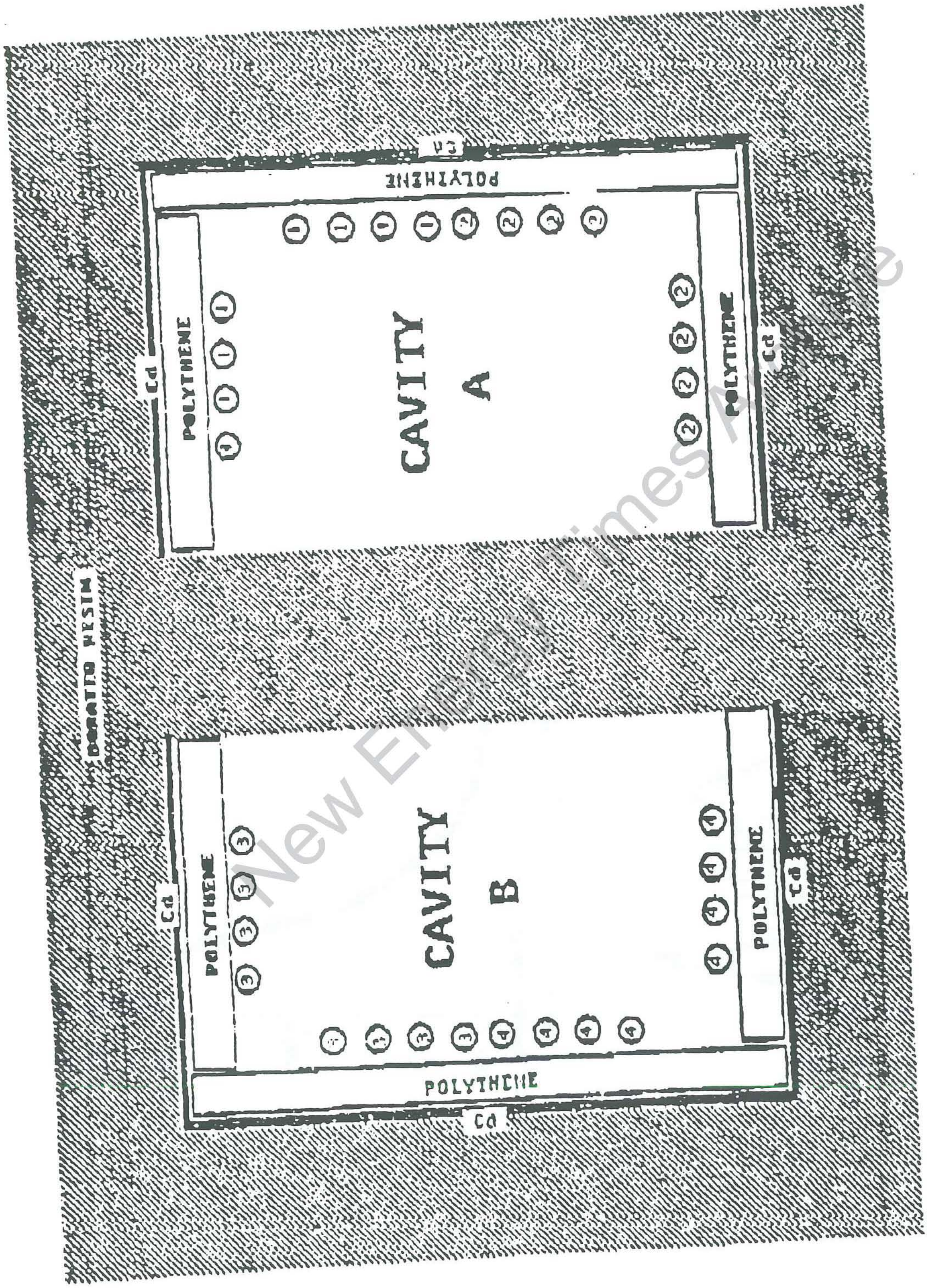
CAVITY A
CAVITY B
POLYTHENE
POLYTHENE
POLYTHENE
POLYTHENE
POLYTHENE
POLYTHENE
Cd
Cd
Cd
Cd
Cd
Cd
BORATED RESIN
1
2
3
4

FIG 2

EXPERIMENT NO 1 JET COUNTER. $\tau_i = 1000$

sum of 6 probe detectors (2/May/89)

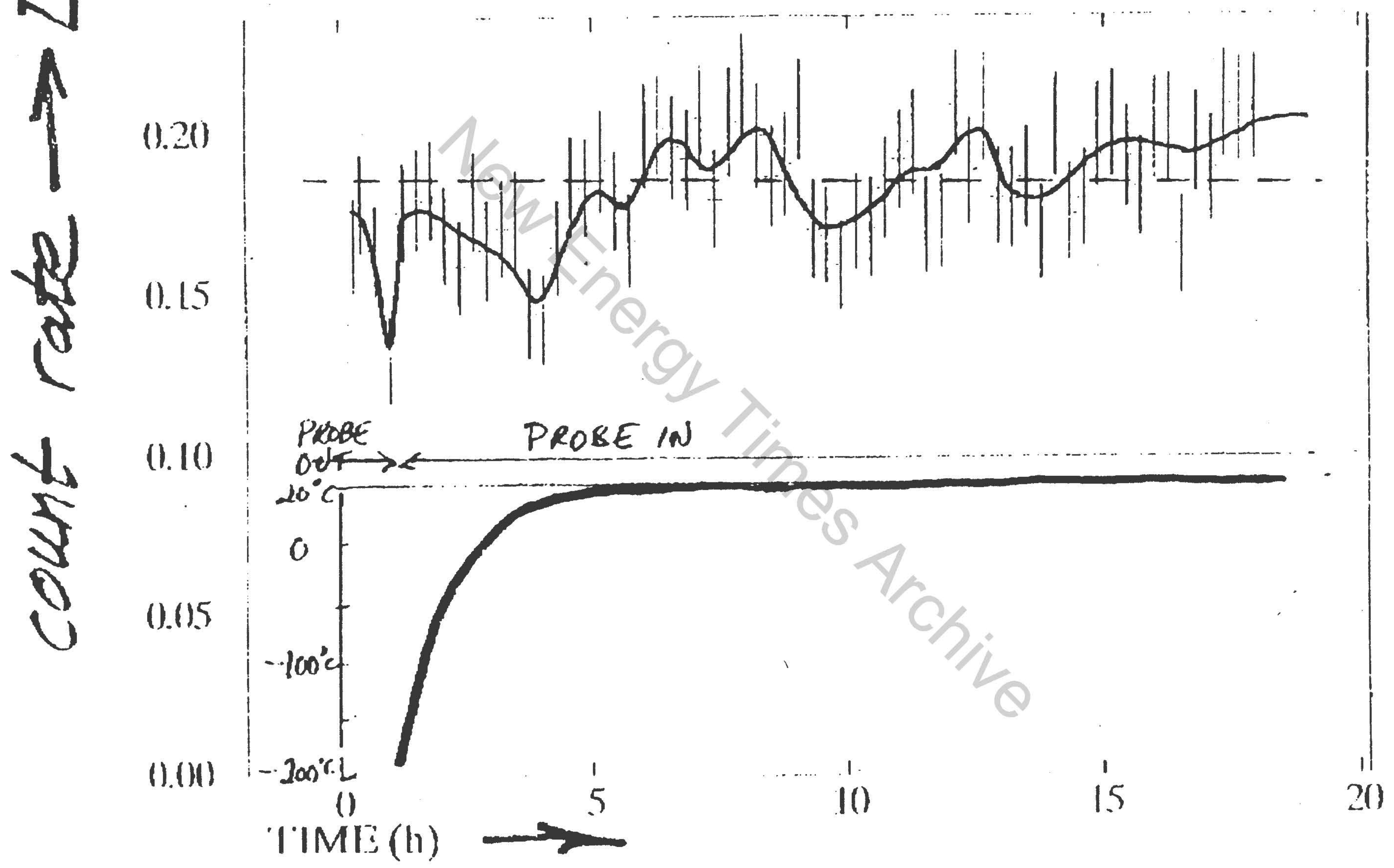

FIG 3

Average D/12 = .016

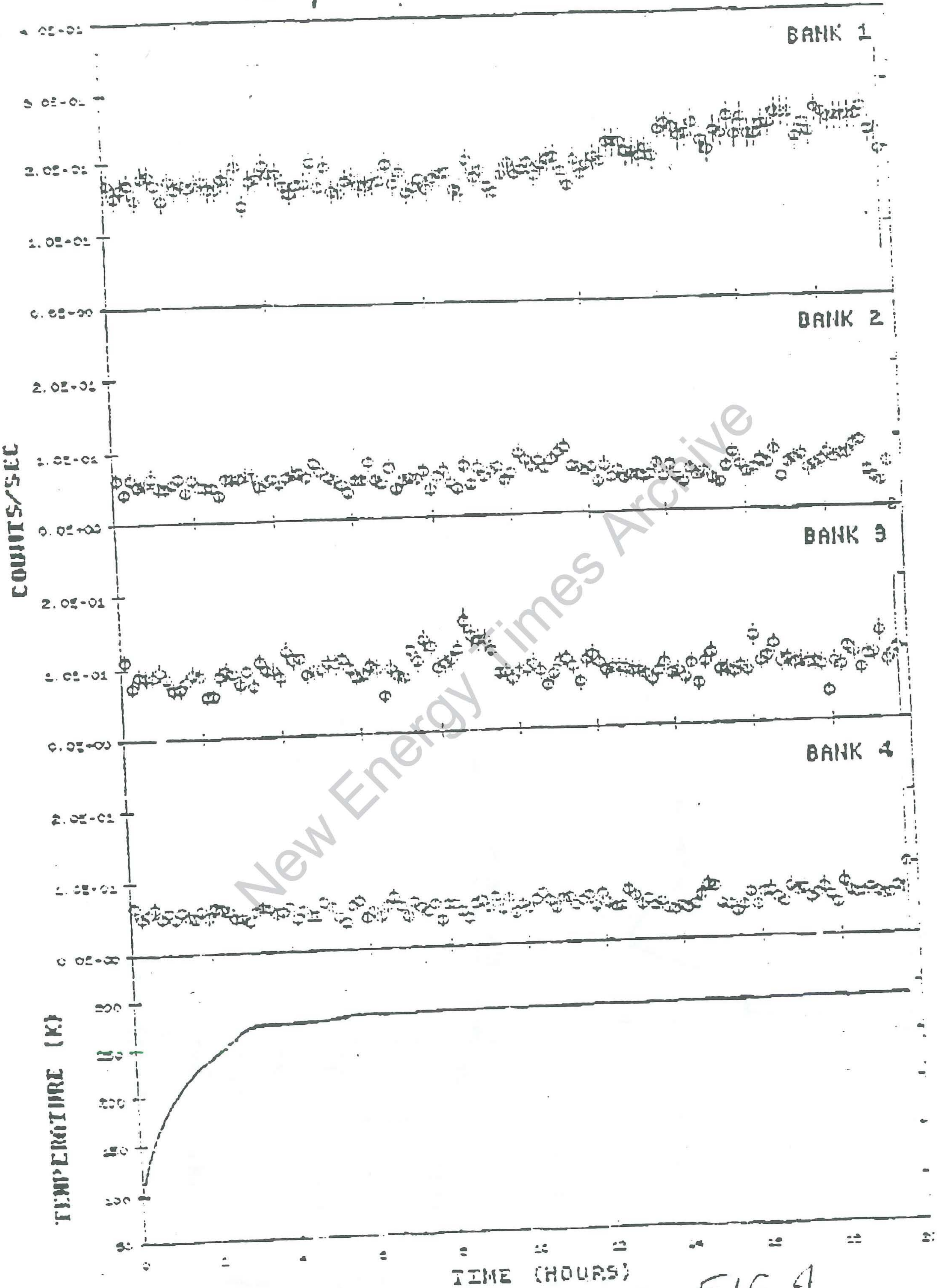

FIG 4

EXPERIMENT No 5 JET COUNTER. $\tau_i = 500$ s

sum of 6 probe detectors (15/May/89) (500 s)

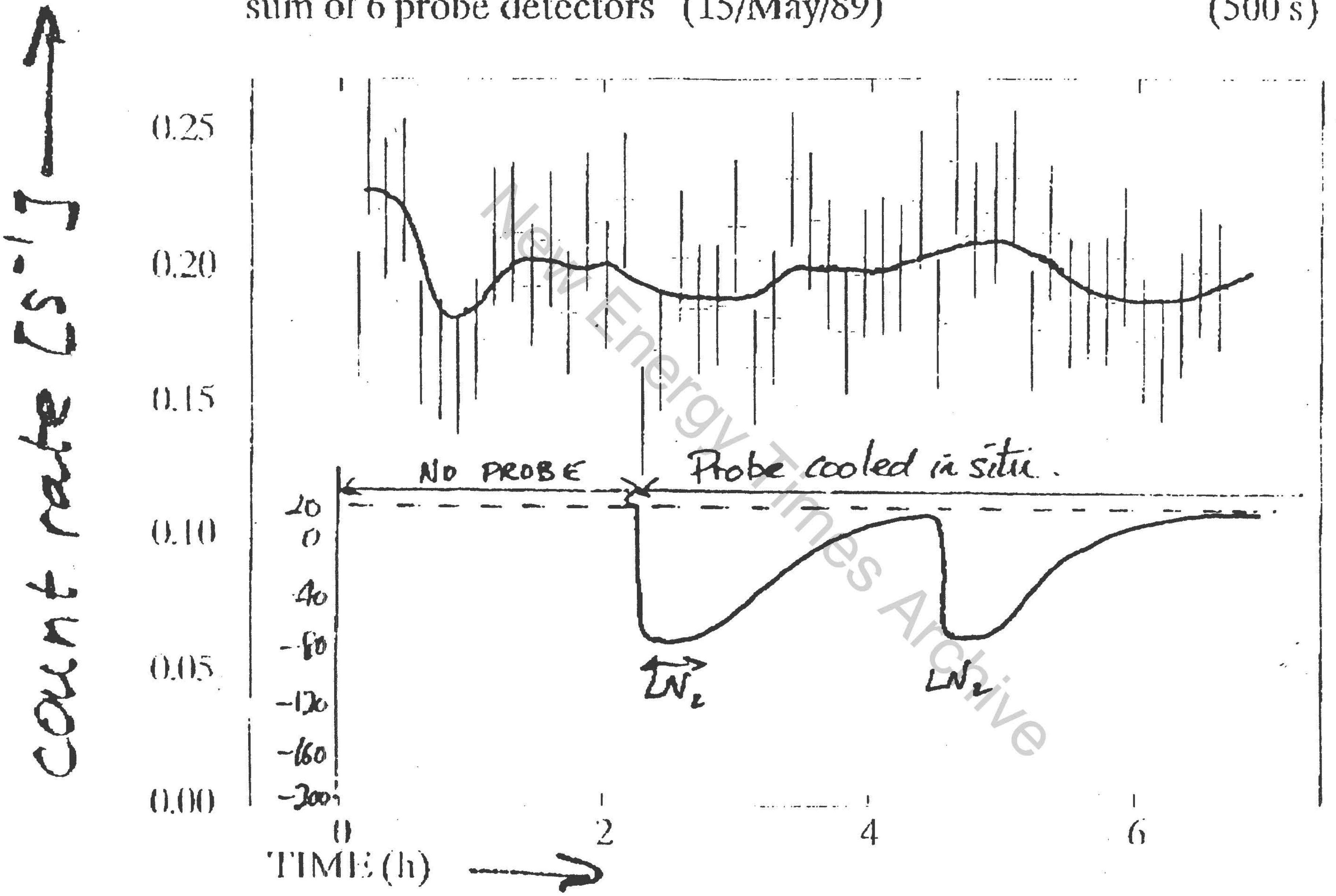

FIG 5

EXPERIMENT No 6 HARWELL COUNTER

Average D/Ti = 0·14

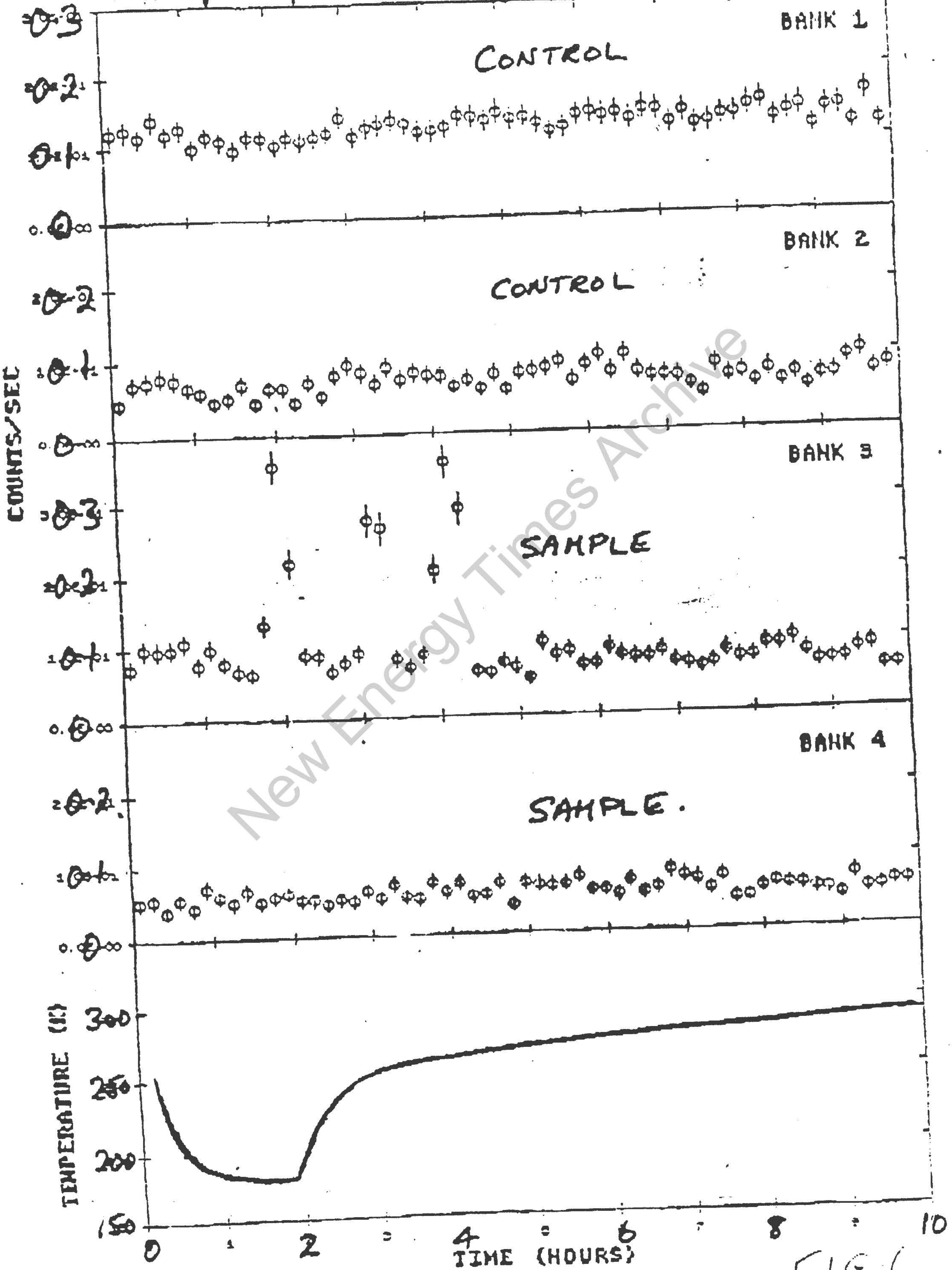

FIG 6.

OAK RIDGE NATIONAL LABORATORY
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August 31, 1989

MATERIALS RES. LAB.
SEP 5 1989
RECEIVED

Dr. Howard K. Birnbaum
Office of the Director
Materials Research Laboratory
104 South Goodwin Avenue
Urbana, Illinois 61801

Dear Dr. Birnbaum:

In response to your request of July 15, 1989, enclosed are cold fusion reports from the four active experimental groups at the Oak Ridge National Laboratory (ORNL).

If you have any questions, please contact me at (615)574-4321.

Sincerely,

Bill R. Appleton

Bill R. Appleton
Associate Director

BRA:jcm

cc: J. B. Ball
W. Fulkerson
R. K. Genung
M. L. Poutsma
M. W. Rosenthal
M. J. Saltmarsh
J. Sheffield
J. O. Stiegler
A. W. Trivelpiece

MATERIALS USED IN COLD FUSION EXPERIMENTS

PRINCIPAL INVESTIGATOR: C. D. Scott

ORGANIZATION: Oak Ridge National Laboratory, Chemical Technology Division

SHORT DESCRIPTION OF TYPE OF EXPERIMENT:

Electrochemical cells utilizing Pd cathodes and Pt anodes in 0.1 to 0.2 *N* LiOD were used. The electrolysis cell was insulated and a cooling jacket with circulating water used for heat removal. The neutron flux and gamma ray spectra were measured, and periodic electrolyte sampling for T was carried out. Electrical current densities of 100 to 600 mA/cm^2 Pd were used. In all completed experiments the cells were open, allowing the evolved D_2 and O_2 gasses to leave the cell. In the current, uncompleted experiment, an internal recombiner is being used so that the system is completely closed.

RESULTS AND COMMENTS:

In some of the open-system experiments, apparent excess power was detected for periods of several hours, usually in the range of 5 to 10%. However, during one 12-hour period an apparent imbalance of up to 50% was seen. These excursions, which were transitory, appeared after the current density was increased. They could be extended by perturbing the system, for example changing the electrolyte temperature or increasing the electrolyte concentration. There were two occasions, uncorrelated with any excess power observations, where the neutron detector count rate exceeded average background values by greater than three standard deviations. Recent, very preliminary results from a closed system, which includes a recombiner, are also indicating a power imbalance of ~5%, although this experiment is not yet complete.

I. MATERIALS USED FOR ELECTROCHEMICAL EXPERIMENTS (please complete one sheet for each experiment)

	CATHODES	ANODES (Corresponding)
MATERIAL	Pd	Pt wire
PURITY	99.9%	99.9+%
ALLOYING ELEMENTS	None	None
SOURCE OF MATERIAL	Materials Research Corp.	Englehard Corp.
PREPARATION CAST OR WROUGHT ANNEALED ATMOSPHERE VACUUM SPECIAL TREATMENT	Cast in Ar, swaged to appropriate diam, then annealed at 950°C under vacuum for 4 hours	
CHARACTERIZATION STRUCTURAL CHEMICAL BEFORE OR AFTER USE METHODS RESULTS	0.28-cm diam x 8-cm cylinder	24 ga wire
NOTABLE OBSERVATIONS	Periods of several hours of apparent excess power in the range of 5 to 10% were observed after changes to experimental conditions.	

D/METAL RATIO ATTAINED

EXPERIMENT YIELDED HEAT __X__ yes ______ no

NEUTRONS ______ yes __X__ no

TRITIUM ______ yes __X__ no

HELIUM ______ yes __X__ no

I. MATERIALS USED FOR ELECTROCHEMICAL EXPERIMENTS (please complete one sheet for each experiment)

	CATHODES	ANODES (Corresponding)
MATERIAL	Pd, 0.28-cm diam x 9 cm	28 ga Pt wire
PURITY	99.9%	99.9+%
ALLOYING ELEMENTS	None	None
SOURCE OF MATERIAL	Materials Research Corp.	Englehard Corp.
PREPARATION CAST OR WROUGHT ANNEALED ATMOSPHERE VACUUM SPECIAL TREATMENT	Cast in Ar, swaged to appropriate diam	
CHARACTERIZATION STRUCTURAL CHEMICAL BEFORE OR AFTER USE METHODS RESULTS	0.28-cm diam x 9-cm cylinder	28 ga wire
NOTABLE OBSERVATIONS	Neutron count rate exceeded three standard deviations of the average background during a 4-hour period.	

D/METAL RATIO ATTAINED

EXPERIMENT YIELDED HEAT ______ yes __X__ no
NEUTRONS ______ yes __X__ no
TRITIUM ______ yes __X__ no
HELIUM ______ yes __X__ no

MATERIALS USED IN COLD FUSION EXPERIMENTS

PRINCIPAL INVESTIGATOR: D. P. Hutchinson

ORGANIZATION: Oak Ridge National Laboratory, Physics Division

SHORT DESCRIPTION OF TYPE OF EXPERIMENT:

Four calorimetry cells were operated for a period of over 1800 hours with two cells using 6.35-mm diam. x 10-cm long palladium cathodes in a 0.2 M ^{6}LiOD electrolyte, one cell with a similar cathode in a 0.1 M ^{6}LiOD electrolyte solution and one cell containing a cast 1.27-cm diam. x 10-cm palladium rod in a 0.2 M electrolyte. All cells were constructed with an electrolyte volume of 300 cm^3 and a 54 mm o.d. quartz envelope. No D_2/O_2 recombination was assumed. All of the cells contained a platinum wire spiral wound anode with a diameter of 30 mm. Two of the cells had 6.35 mm palladium rod electrodes precharged in D_2 gas to a stoichiometry of 0.6.

RESULTS AND COMMENTS:

The cells were operated at a current density of 50 mA/cm^2 for 48 hours and then at a current density of 250 mA/cm^2 for over 1800 hours. Three of the cells have remained in power balance within the experimental uncertainty of ±1 watt for the duration of the experiments. However, one of the cells, containing one of the non-precharged rods, exhibited an apparent power deficit of approximately 2 watts for the first 75 hours of operation, followed by an apparent power excess of approximately 3 watts for a 600-hour period beginning 150 hours after the beginning of the experiment. From 75 hours to 150 hours, the cell was in power balance. Shortly after the excess power was indicated, the cell was placed in a neutron counter containing a pair of NE213 scintillator detectors with pulse shape discrimination. The neutron emission level of the cell was determined to be less than 1×10^{-24} neutrons/s/D-D pair. Various changes were made to the cell during the period of apparent imbalance to improve the calorimetry measurement and to determine the effect of changes on the observation. The imbalance was not significantly affected by the bath temperature changes between 13 and 20°C, but disappeared with a reduction in temperature to 5°C. The apparent excess reappeared when the temperature was raised to 13°C, disappeared when the temperature of the bath was once again lowered to 5°C, and did not return after a temperature increase to 13°C. Subsequently, this cell has remained in power balance for 1100 hours. We are planning a thorough material analysis of the rods following the termination of these initial experiments in September 1989 and attempting to reproduce these observations.

I. MATERIALS USED FOR ELECTROCHEMICAL EXPERIMENTS (please complete one sheet for each experiment)

	CATHODES	ANODES (Corresponding)
MATERIAL	Palladium (6.35-mm diam x 10-cm long rod)	Platinum wire, #20 gauge
PURITY	99.96%	
ALLOYING ELEMENTS	None	
SOURCE OF MATERIAL	Johnson-Matthey	
PREPARATION **CAST OR WROUGHT** **ANNEALED** **ATMOSPHERE** **VACUUM** **SPECIAL TREATMENT**	Wrought Vacuum annealed @ 900°C for 2 hours	
CHARACTERIZATION **STRUCTURAL** **CHEMICAL** **BEFORE OR AFTER USE** **METHODS** **RESULTS**	In progress	
NOTABLE OBSERVATIONS	The cell that exhibited an apparent power imbalance was accidentally contaminated with a stainless steel screw in the electrolyte during assembly. It was not possible to remove the screw after the experiment began, and it remained in the cell for the entire duration. The significance of this is not known.	
D/METAL RATIO ATTAINED	As yet undetermined	

EXPERIMENT YIELDED HEAT _____ yes _____ no (See text)
NEUTRONS _____ yes __X__ no
TRITIUM _____ yes __X__ no
HELIUM _____ yes __X__ no

MATERIALS USED IN COLD FUSION EXPERIMENTS

PRINCIPAL INVESTIGATOR: E. L. Fuller, Jr.

ORGANIZATION: Oak Ridge National Laboratory, Metals and Ceramics Division

SHORT DESCRIPTION OF TYPE OF EXPERIMENT:

A power calorimeter designed around a 40-gallon (water) temperature bath, controlled to 0.01°C or better, is currently in operation with four cells. Up to eight cells can be accommodated.

Each cell holds 75 mL of electrolyte (either 0.1 N $^6LiOD/D_20$ or 0.1 N $^6LiOH/H_2O$), and is equipped with a mechanical stirrer and calibration heater. The calorimeter cells can be operated over three power output ranges: (1) with an air jacket for very low power, (2) with a water jacket for intermediate power output, and (3) with no jacket (i.e., direct connection of the cell to the bath) for the highest power output.

RESULTS AND COMMENTS:

In this experiment, the cells are brought on-line two at a time; one with light water and one with heavy water. The current is connected in series between the two cells. This has the advantage of not only subjecting the cells to identical currents, but also providing a check on the electrolysis rate and the amount of makeup water required.

No excess heat or tritium (above background) has been detected in these experiments to date.

I. MATERIALS USED FOR ELECTROCHEMICAL EXPERIMENTS (please complete one sheet for each experiment)

	CATHODES	ANODES (Corresponding)
MATERIAL	Palladium	Ni Rod
PURITY	99.95%	
ALLOYING ELEMENTS	None	
SOURCE OF MATERIAL	Johnson-Matthey	
PREPARATION CAST OR WROUGHT	Wrought	
ANNEALED ATMOSPHERE VACUUM SPECIAL TREATMENT	Annealed at 600°C for 4 hours	Annealed at 600°C for 4 hours
CHARACTERIZATION STRUCTURAL CHEMICAL BEFORE OR AFTER USE METHODS RESULTS	In progress	
NOTABLE OBSERVATIONS	During the initial stages of electrolysis, a fine, black powder (probably nickel oxide) formed in the cell.	
D/METAL RATIO ATTAINED	Undetermined; experiment in progress.	

EXPERIMENT YIELDED HEAT ______ yes ___X___ no

NEUTRONS ______ yes ___X___ no

TRITIUM ______ yes ___X___ no

HELIUM ______ yes ___X___ no

I. MATERIALS USED FOR ELECTROCHEMICAL EXPERIMENTS (please complete one sheet for each experiment)

	CATHODES	ANODES (Corresponding)
MATERIAL	Palladium	Pt wire
PURITY	>99.9%	
ALLOYING ELEMENTS	None	
SOURCE OF MATERIAL	In-house	
PREPARATION **CAST OR WROUGHT** **ANNEALED** **ATMOSPHERE** **VACUUM** **SPECIAL TREATMENT**	Cold-cast under an Ar atmosphere in a copper mold	
CHARACTERIZATION **STRUCTURAL** **CHEMICAL** **BEFORE OR AFTER USE** **METHODS** **RESULTS**	In progress	
NOTABLE OBSERVATIONS	With the calorimeter design employed in this experiment, mechanical stirring is essential for obtaining a correct cell output power from the thermistor response (even at 200 mA/cm^2).	
D/METAL RATIO ATTAINED	Undetermined; experiment in progress.	

EXPERIMENT YIELDED HEAT ______ yes ___X___ no

NEUTRONS ______ yes ___X___ no

TRITIUM ______ yes ___X___ no

HELIUM ______ yes ___X___ no

MATERIALS USED IN COLD FUSION EXPERIMENTS

PRINCIPAL INVESTIGATOR: E. L. Fuller, Jr.

ORGANIZATION: Oak Ridge National Laboratory, Metals and Ceramics Division

SHORT DESCRIPTION OF TYPE OF EXPERIMENT:

Six electrochemical cells using a variety of cathodes (different materials, sizes, or treatments) were. operated in an arrangement suitable for neutron counting with BF_3 detectors. The cathodes for the six cells were as follows: (1) two cold-cast, swaged 3.1-mm-diam by 5-cm palladium rods, (2) one cold-cast 6.25-mm-diam by 5-cm palladium rod, (3) one 44-g cold-cast palladium "button," (4) one cold-cast 10.9-mm-diam by 3-cm palladium rod, and (5) one cold-cast 6.25-mm-diam by 5-cm titanium rod. The anodes were either platinum or platinum/rhodium wire and the electrolyte was 0.1 N ^6LiOD. All cells were operated at current densities ranging from 25 to 300 mA/cm^2.

RESULTS AND COMMENTS:

Initially, a single BF_3 detector (~2% efficiency for Cf252 fission neutrons with ca. 200 counts per hour background), immersed in a water moderating bath, was used to monitor possible neutron emission from six surrounding electrochemical cells. After having observed an increase in the count rate of this detector, lasting about 18 hours and persisting even with the electrochemical cells removed from the bath, a second BF_3 detector was introduced to monitor the background level. Pulse height discrimination was used with both detectors to reduce noise counts, and a multichannel analyzer was used to observe the overall BF_3 output. Subsequently two unexplained increased in the BF_3 detector count rate were recorded while the experiment was unattended. In both of these instances the background monitor detector count rate remained constant. In one of these instances the count rate increased for about 24 hours. This incident was somewhat similar to the one that had led earlier to the introduction of the background monitor detector and a subsequent one in which the detector became very noisy for about 24 hours (the source of this noise was not discovered. In the second instance of increased count rate, two increases were recorded, lasting approximately 45 and 60 minutes, respectively, with the background monitor detector showing no corresponding increases. Such large increases in recorded count rates wee occasionally observed in both counters and were caused by microphonics. Although the recorded increases in count rate while the experiment was unattended could have been caused by neutrons from the cells, not enough control existed in the experiment to conclude that this was definitely the case. The cell with a 44 gram electrode exploded (presumably $D_2 + O_2$) and since that date neither of the BF3 detectors have shown any variation above background (for about two months).

I. MATERIALS USED FOR ELECTROCHEMICAL EXPERIMENTS (please complete one sheet for each experiment)

	CATHODES	ANODES (Corresponding)
MATERIAL	Palladium, Titanium	Platinum or Platinum/Rhodium
PURITY	≥99.9%	
ALLOYING ELEMENTS	None	
SOURCE OF MATERIAL	In-house	
PREPARATION CAST OR WROUGHT ANNEALED ATMOSPHERE VACUUM SPECIAL TREATMENT	Cold-cast under Ar using copper molds. 3.1-mm rods were swaged from a single 6.25-mm rod.	
CHARACTERIZATION STRUCTURAL CHEMICAL BEFORE OR AFTER USE METHODS RESULTS	B-phase slowly undergoing a phase transition, but with no detectable α-phase (by x-ray diffraction). One electrode showed a large rhenium level after use (by glow-discharge mass spectrometry).	
NOTABLE OBSERVATIONS	The after-use palladium electrodes examined to date have shown a remarkable ability to retain deuterium. After several months, the D/Pd ratio in one electrode remained above 0.5.	
D/METAL RATIO ATTAINED	≥0.82 for Pd; not determined for Ti.	

EXPERIMENT YIELDED HEAT ______ yes ___X___ no
NEUTRONS ______ yes ______ no (see text)
TRITIUM ______ yes ___X___ no
HELIUM ______ yes ___X___ no

MATERIALS USED IN COLD FUSION EXPERIMENTS

PRINCIPAL INVESTIGATOR: J. G. Blencoe

ORGANIZATION: Oak Ridge National Laboratory, Chemistry Division

SHORT DESCRIPTION OF TYPE OF EXPERIMENT:

Investigation of reactions between high-purity palladium and deuterium at high gas pressures and low temperatures.

RESULTS AND COMMENTS:

A series of experiments were conducted to elucidate reactions between Pd and D_2 at high pressures and low temperatures. In our initial Pd-D_2 experiment, 0.7 grams of 0.1-mm thick palladium ribbon (Table 1) was wrapped around the tip of the lower (sample) thermocouple and sheathed with platinum foil. Pressurization of this sample to 380 MPa with 99.87% D_2 gas produced a rapid temperature rise (from 27 to 60°C) that was much larger than a simultaneous temperature rise (from 27 to 32°C) recorded by the reference thermocouple. This thermal anomaly decayed to the bath temperature after 12 minutes. During and for five days after this pressurization, the neutron flux was monitored at sampling times ranging from 6 seconds to 10 minutes. No sustained neutron flux above background was observed. Subsequent pressurizations of D_2 gas alone and 0.7 grams of palladium with H_2 gas produced thermal effects similar to the initial run, indicating that the thermal anomaly observed during our first Pd-D_2 experiment can be attributed to (1) PV work accompanying gas pressurization, (2) heat released during the formation of palladium deuteride, and (3) the somewhat different geometries of the sample and reference thermocouples.

The pressure vessel was then packed with 7.0 grams of palladium in the form of (1) ~1 gram of 0.1-mm thick ribbon wrapped around the sample thermocouple, and (2) ~6 grams of 3-mm x 3-mm cut pieces of 0.1-mm thick ribbon filling the space between the sample and reference thermocouples. Upon initial pressurization to 380 MPa with D_2 gas, thermal effects similar to those described above were observed. During the next three days, the temperature of the vessel was (1) reduced to -78°C using dry ice, and subsequently (2) allowed to warm slowly to room temperature. This was done because several investigators (e.g., Perminov et al., 1952) have reported greatly enhanced solubility of hydrogen in palladium at cryogenic temperatures. Finally, the sample was depressurized to a 20 micron vacuum at room temperature for one day and repressurized to 350 MPa for two days. As in the first Pd-D_2 experiment, no sustained neutron flux above background was observed.

I. MATERIALS USED FOR GASEOUS CHARGING EXPERIMENTS (please complete one sheet for each experiment)

MATERIAL	Palladium
PURITY	99.97 wt. %
ALLOYING ELEMENTS	See attached table.
SOURCE OF MATERIAL	Martin Marietta Energy Systems Stores, Y-12 Plant, Oak Ridge, Tennessee
PREPARATION	
CAST OR WROUGHT	See attached table.
ANNEALED	
ATMOSPHERE	
VACUUM	
SPECIAL TREATMENT	
CHARACTERIZATION	
STRUCTURAL	None.
CHEMICAL	See attached table.
BEFORE OR AFTER USE	Before.
METHODS	See attached table.
RESULTS	See attached table.
NOTABLE OBSERVATIONS	Deuterium continued to effuse from the palladium long after experimentation.
D/METAL RATIO ATTAINED	

EXPERIMENT YIELDED HEAT	X* yes	no	don't know
NEUTRONS	yes	X no	don't know
TRITIUM	yes	no	X don't know
HELIUM	yes	no	X don't know

*Heat released is believed to be entirely chemical (not nuclear).

Table 1. Analysis of 99.97% Palladium Ribbon[a,b]

Ag	6	As	0.7	Au	1	B	12	Ba	<0.2	Be	0.20	Bi	<0.1
Br	<0.04	Ca	73	Cd	<0.20	Co	0.02	Cs	<0.03	Cu	9	Fe	19
Ga	<0.03	Ge	<0.02	Hf	<0.05	Hg	<0.08	In	<0.01	Ir	3	K	0.50
Mg	0.70	Mo	2	Na	0.07	Nb	0.20	Ni	3	Os	<0.05	P	0.30
Pb	0.7	Pt	52	Rb	<0.01	Re	<0.02	Rh	29	Ru	<0.06	S	3
Sb	<0.05	Sc	0.02	Se	<0.01	Si	54	Sn	<0.30	Sr	0.03	Ta	<5
Te	5	Th	0.06	Ti	2	Tl	<0.02	U	0.20	W	0.60	Y	<0.02
Zn	2	Zr	4	Cl	0.40	F	<0.01	I	<0.03	Ce	<0.10	Dy	<0.04
Er	<0.04	Eu	<0.02	Gd	<0.05	Ho	<0.01	La	<0.04	Lu	<0.01	Nd	<0.05
Pr	<0.01	Sm	<0.04	Tb	<0.01	Tm	<0.01	Yb	<0.04				

[a] Concentrations of all trace elements reported in ppm.

[b] Analyzed by DC-arc spectrograph at the Y-12 Plant, Oak Ridge, TN. Masked elements include Al, Cr, Mn, and V. Prior to use in experimentation, the ribbon was: cleaned in concentrated aqua regia; heated to 600°C under high vacuum (10^{-5} torr); exposed to 0.05 MPa D_2 gas at 600°C for 15 minutes; held at 600°C under high vacuum (10^{-5} torr) for one hour; cooled back to room temperature; and finally, stored under 99.999% argon. Additionally, to preclude surface contamination prior to experimentation, the ribbon was loaded into the pressure vessel under 99.999% argon.

MATERIALS USED IN COLD FUSION EXPERIMENTS

PRINCIPAL INVESTIGATOR: J. G. Blencoe

ORGANIZATION: Oak Ridge National Laboratory, Chemistry Division

SHORT DESCRIPTION OF TYPE OF EXPERIMENT:

Investigation of reactions between high-purity titanium and deuterium at high gas pressures and low temperatures.

RESULTS AND COMMENTS:

A single Ti-D_2 experiment has been conducted to test the claim that special disequilibrium pressure-temperature conditions will induce cold fusion in Ti-D_2 samples.

Starting materials for the Ti-D_2 experiment were (1) 1.6 mm-diameter titanium wire that was chemically polished in an acid bath prior to experimentation (Table 1), and (2) high-purity D_2 gas. The titanium wire (a total of 9 grams) was cut into 0.5- to 2.5-cm lengths before being subjected to high D_2 pressure. To prevent surface oxidation, the titanium wire was stored and transferred under 99.999% argon.

During the Ti-D_2 experiment, data were collected on pressure, temperature, and detector counts. In detail, the sequence of events was as follows: (1) pressurization to 380 MPa; (2) after approximately 29 hours (to compensate for a slow gas leak), repressurization to 380 MPa; (3) cooling to -78°C using dry ice, which produced a drop in pressure from 380 to 320 MPa; (4) slow warming to approximately 10°C over a 20-hour period, (5) depressurization to 80 MPa; (6) cooling to -196°C using liquid nitrogen, which produced a drop in pressure from 80 to 40 MPa; (7) slow warming to approximately -120°C over a 21-hour period, which produced an increase in pressure from 40 to 60 MPa; (8) rapid warming to 27°C over a 6-hour period, which produced an increase in pressure from 60 to 70 MPa; and finally (9) rapid cooling to -196°C, followed by rapid warming to 27°C, all within the space of an hour. After 105 hours of experimentation, the D_2 was vented from the pressure vessel and a vacuum pump was used to remove any residual gas.

The average detector count rate for the 105 hours of experimentation was 532.1 counts/hour. Approximately 80 hours after the experiment began, the count rate increased to ~590 counts/hour and remained at that level for about 5 hours. This increase cannot be due to random fluctuations in the average count rate and is potentially significant. If the increase can be attributed to neutrons emitted by the Ti-D_2 sample, this would correspond to an emission rate of ~1000 neutrons/hour.

However, because we cannot completely verify that our neutron detectors were operating properly during this 5-hour period, it cannot be claimed that cold fusion neutrons were observed. We are planning to repeat our Ti-D_2 experiment with an improved detector system where (1) moderated neutrons will be detected by two totally independent detector systems, (2) the background count rate will be monitored continuously by a similar and independent detector system placed nearby, and (3) additional shielding will be provided in an attempt to improve the neutron sensitivity of our detector systems.

I. MATERIALS USED FOR GASEOUS CHARGING EXPERIMENTS (please complete one sheet for each experiment)

MATERIAL	Titanium
PURITY	99.91 wt. %
ALLOYING ELEMENTS	See attached table.
SOURCE OF MATERIAL	Commercial source (See attached table.)
PREPARATION CAST OR WROUGHT ANNEALED ATMOSPHERE VACUUM	None.
SPECIAL TREATMENT	See attached table.
CHARACTERIZATION	
STRUCTURAL	None.
CHEMICAL	See attached table.
BEFORE OR AFTER USE	Before.
METHODS	See attached table.
RESULTS	See attached table.
NOTABLE OBSERVATIONS	No visible evidence of any reaction between the titanium and deuterium.
D/METAL RATIO ATTAINED	Not determined.

EXPERIMENT YIELDED HEAT	____	yes	X	no	____	don't know
NEUTRONS	____	yes	X	no	____	don't know
TRITIUM	____	yes	____	no	X	don't know
HELIUM	____	yes	____	no	X	don't know

Table 1. Analysis of 99.91% Titanium Wire[a,b]

C	35.0	N	15.0	O	500.0	Mg	<5.0	Si	<5.0	Al	20.0	S	10.0
Ca	5.0	V	5.0	Cr	40.0	Mn	30.0	Fe	150.0	Ni	40.0	Cu	30.0
Sn	10.0	Pb	20.0	Bi	<10.0								

[a] Concentrations of all trace elements reported in ppm.

[b] Lot analysis reported by vendor (#22/58107, Materials Research Corp., Orangeburg, NY). Prior to use in experimentation, the wire was chemically polished in an acid bath (nitric + lactic + hydrofluoric acid in a 5:5:4 ratio) to remove all surficial titanium oxide.

Lawrence Berkeley Laboratory
1 Cyclotron Road Berkeley, California 94720
(415) 486-4000 • FTS 451-4000

MATERIALS RES. LAB.
AUG 21 1989
RECEIVED

August 18, 1989

Professor Howard K. Birnbaum
Materials Research Laboratory
104 South Goodwin Ace.
Urbana, IL 61801

Dear Prof. Birnbaum:

Enclosed is my response to your request on 15 July for details on the materials aspects of our Cold Fusion studies. Other investigators from LBL will be replying to you individually. Most of the Pd cathodes used on LBL/UCB experiments came from my laboratory, where we prepared cast ingots from high purity Pd "sponge" or "shot". We (at LBL and/or UCB) have not done any calorimetry, but have concentrated on the detection of fusion products, including neutrons, tritium, helium, x-rays, or energetic charged particles. The results have been entirely negative.

Sincerely,

Philip N. Ross
Senior Scientist

cc: G. Rosenblatt
    D. Shirley

II. MATERIALS USED FOR GASEOUS CHARGING EXPERIMENTS (please complete one sheet for each experiment)

MATERIAL	Palladium
PURITY	5N "shot" from Englehard
ALLOYING ELEMENTS	None
SOURCE OF MATERIAL	Englehard
PREPARATION CAST OR WROUGHT ANNEALED ATMOSPHERE VACUUM SPECIAL TREATMENT	Cast in boron nitride in high purity argon atmosphere Machined into tubes 1 mm wall thickness, e-beam welded to ceramic-metal transition, vacuum annealed (both inner and outer surfaces) at 600 C.
CHARACTERIZATION STRUCTURAL CHEMICAL BEFORE OR AFTER USE METHODS RESULTS	Surface analysis before and after use by Auger electron spectroscopy and Ruthford backscattering (RBS).

Lithiation of Pd occurs during electrolysis in LiOH(D), causing high ovcerpotentials on outer surface but no effect on inner potential, i.e. thermodynamic activity of hydrogen or deuterium in bulk lattice.

NOTABLE OBSERVATIONS

D / METAL RATIO ATTAINED 0.8 ± 0.02

EXPERIMENT YIELDED HEAT	______yes	______no	N.A.
NEUTRONS	______yes	____X_no	
TRITIUM	______yes	____X_no	
HELIUM	______yes	____X_no	

MATERIALS USED IN COLD FUSION EXPERIMENTS

PRINCIPAL INVESTIGATOR: Philip N. Ross

ORGANIZATION: Lawrence Berkeley Laboratory

SHORT DESCRIPTION OF TYPE OF EXPERIMENT: Electrolytic charging of palladium cathodesin KOH(D) and LiOH(D). Palladium is in form of a tube machined from cast ingot and e-beam welded to pressure "tap.", i.e. strain gauge. Equilibrium pressure of $H_2(D_2)$ in the Pd measured as a function of overpotential and current density during electrolysis. Electrolysis done in closed cell with recombination catalyst. Electrolyte analyzed for tritium, Pd analyzed for He in post-mortem.

RESULTS AND COMMENTS: See enclosed abstract. No production of tritium or helium observed at any condition of electrolysis, including current densities as high as 1 A/cm^2.

LAWRENCE BERKELEY LABORATORY
Bldg.: 2 Room: 110 Ext.: 6226

ABSTRACT OF RECENT NEWS PAPER FOR COLD FUSION SESSION
THE ELECTROCHEMICAL SOCIETY FALL MEETING
HOLLYWOOD, FL - OCTOBER 15-20, 1989

"In-Situ Measurements of the H(D) Thermodynamic Activity and Stoichiometry in Pd Cathodes During Electrolysis"

Philip Ross and Harvey Sokol
Materials and Chemical Sciences Division
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A variation of the classic experiments on Pd charging by Frumkin[1] were performed in alkaline electrolytes. Membrane potentials were measured using Pd diffusion tubes having a strain gauge and reference electrode sealed in the "backside" (zero current) of the tube. Frontside (current carrying) and backside potentials and inner hydrogen (deuterium) pressures were measured in 1M KOH(D) and LiOH(D). In KOH, the backside potentials were identical to those reported by Frumkin[1] in 1M H_2SO_4, e.g. $\eta = 42$ mV or $p_{H2} = 21.5$ atm, corresponding to a Pd/H stoichiometry of 0.82 ± 0.02. This activity and stoichiometry was independent of current density, even for current densities as high as 1 A/cm^2. In KOD, the maximum stoichiometry was slightly lower, 0.78 ± 0.02. In LiOH(D), very different behavior was observed for the frontside potentials, which became very cathodic ($\eta = 1000$ mV) at high current density without any corresponding change in the backside potential. Post-mortem analysis of the Pd cathode surface by RBS revealed penetration of Li into the surface region (1-10 μm) during electrolysis at high current density. It is suggested that Fleischmann et al.[2] misinterpreted very negative Pd cathode potentials as indicating very high H(D) activity, which our measurements indicate is not the case.

[1] A. Frumkin and N. Aladyalova, Acta Physicochim. USSR 19, 1(1944)
[2] M. Fleischmann, S. Pons and M. Hawkins, J. Electroanal. Chem. 261, 301(1989)

10/03/89
②

So O^{16} on $Ti^{\cancel{50}\,48}$ $V_a = V_0$ $V_b = 0$

$$V_a' = V_a \frac{16-48}{16+48} = -\frac{V_0}{2}$$

now D on the O^{16}

$$V_a = V_0 \qquad V_b = -\frac{V_0}{2}$$

$$V_a' = \frac{V_0(2-16) - V_0 \times 16}{2+16} = \frac{-30\,V_0}{18} = \underline{\underline{\frac{-5}{3} V_0}}$$

Now $O^{16} \xrightarrow[V_0]{}$ probes $\xleftarrow[-5/3\,V_0]{D}$

$$V_A' = \frac{-5/3\,V_0(2-16) + 2V_0 \times 16}{2+16}$$

$$= \frac{V_0\left[\frac{5}{3}\times 14 + 32\right]}{18} = \underline{\underline{3.074\,V_0}}$$

So instead of 100 eV per amu (200 eV/D), we have $\left(\frac{V_A'}{V_0}\right)^2$ times that -- or $\underline{\underline{1800\text{ eV/D}}}$

For ~~fp~~ $\sigma = 20\times$ for $E = 1.30\times$

we have $\cancel{\log\sigma}\ \ln\sigma = -31\,E^{-1/2}$

$$\Delta\ln\sigma = 3.00 = -31\left[E_1^{-1/2} - E_2^{-1/2}\right]$$

$$= \cancel{-31\,x = \tfrac{1}{2}}\ -31\,[.75 - 0.833]$$

$$= 2.6\ !!$$

Say ~~1800~~ 1.8 keV

~ 1.44 keV